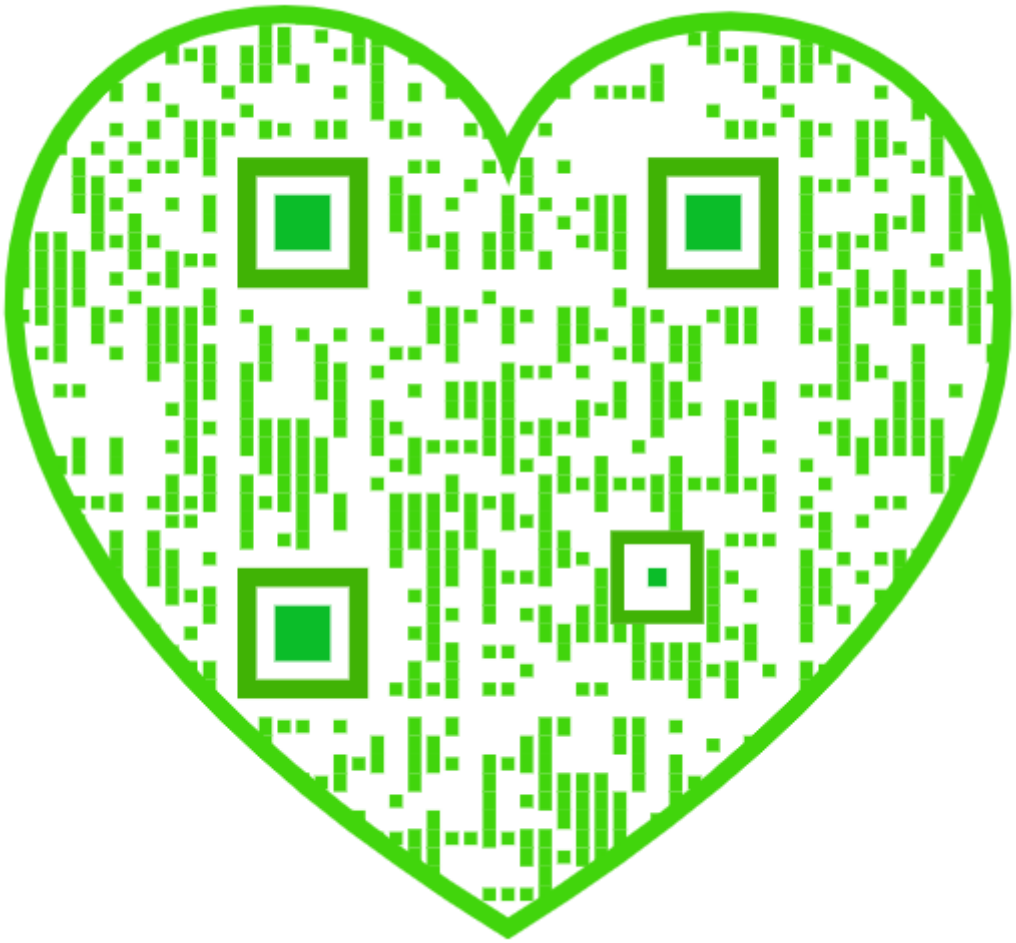

GLUE AND GLUE TESTING

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PREFACE.

In the following pages I have collected the more important facts connected with the manufacture of Glue and allied products together with the experience I have gained in examining various commercial samples during the past ten years which have been used for various purposes. In this work I have been ably assisted by Mr. C. G. Stewart, who has also rendered me considerable help in revising these notes for the press.

SAMUEL RIDEAL.

28 Victoria Street, S.W.,
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CHAPTER I.

CONSTITUTION AND PROPERTIES.

LIKE many commercial terms, the words "glue" and "gelatine," as indicating distinct substances, are not strictly defined. *Gelatine*, from the Latin *gelare*, to congeal, is held to imply, commercially, "animal jelly; glutinous material obtained from animal tissues by prolonged boiling"; this of course would include glue, and accordingly *glue* (Fr. *glu*, later Latin *glus*, "akin to *gluten*, from *gluere*, to draw together".—Webster) is described as "a hard, brittle, brownish gelatine, obtained by boiling to a jelly the skins, hoofs, etc., of animals. . . . The name is also given to other adhesive or viscous substances," like "marine glue," which contains caoutchouc and resins, but no gelatine.

In the ordinary sense, the words are defined with sufficient sharpness by the appearance and the physical characters on which are based the uses of the two products. Gelatine is made in pale or nearly colourless thin sheets, and is used for purposes in which absence of taste, odour and colour, with firmness of jelly and easy solubility, are required. Glue, on the other hand, is employed for its adhesiveness, stiffness and elasticity, and met with in the familiar thick and darker sheets.

To the chemistry of gelatine more attention has been paid than to that of glue, as the former is a purer and more definite substance, and when prepared from different sources, exhibits considerable uniformity in composition

and properties. Neither glue nor gelatine exist ready formed in nature: they are products of the action of heat and water on many nitrogenous animal tissues related to the albuminoids proper, but not identical with them. Allen[1] proposes to avoid the term "albuminoid" wherever possible, and to distinguish the two classes as *proteids*, including fibrin, albumin, casein, etc., and *proteoids*, as gelatin and its congeners.[2] The latter are insoluble in cold water, and in weak acids and alkalies, but some of them swell up in cold, and dissolve in boiling water, the latter more easily when the operation is conducted in a closed vessel, so that the liquid is "superheated," or its boiling point raised by pressure. This group or subclass are called *collagens*, or gelatoids, because their solutions become more or less gelatinous on cooling. They include the following bodies.

Collagen or *Ossein*, the chief component of the white fibres of connective tissue from the skin, tendons, muscles, bones, intestines, and the swimming bladders of fish. It may be prepared by exhausting minced tendons with water, soaking in lime water to dissolve mucin, then washing with water, dilute acetic acid, and again with water, finally gently drying, and exhausting with ether to remove any fat. The product may still contain nuclein and elastin.

Trypsin, a ferment from the pancreas, has the power of digesting "all the tissue elements except the true collagenous

[1] *Commercial Organic Analysis*, 1898, iv., p. 456.

[2] This distinction is convenient, as indicating many group-differences, but cannot imply any fundamental difference in chemical constitution. Maly (*Monats. Chem.*, x., 26), from experiments on the oxidation of albumin and gelatin, considers that "gelatin is as much a proteid as fibrin or casein, and that a classification into albuminoids and proteids cannot be upheld". Buchner and Curtis, by a different treatment (*Berichte*, xix., 850), obtained similar decomposition products from gelatin and albumin, and speak of this as a fresh proof of their analogy in chemical properties.

fibrils," so that it may be used to prepare a very pure collagen. This might in turn be useful as a source of specially pure gelatine.

Bones in the dry state contain about 32 to 33 per cent. of organic matters, consisting mainly of *ossein*—believed to be identical with collagen from tendon and skin—with small quantities of *elastin* (an insoluble nitrogenous body from the membranes lining the Haversian canals, lacunæ, and canaliculi) proteids and nuclein from the bone corpuscles, blood, marrow, nerve-fibres, etc., and a small quantity of fat, even after removal of the marrow. The average composition of undried bone has been given as:—

Water	51·0
Fat	15·7
Ossein, etc.	11·4
Mineral matters	21·9
	100·0

But the percentage of water and fat in this, as in other forms of glue stock, is very variable; therefore, in buying in large quantities, it should be always previously determined.

The inorganic constituents of bone are: calcium phosphate, about 60 per cent.; calcium carbonate, 6 to 7 per cent.; magnesium phosphate, calcium fluoride, and sodium chloride, 1 to 2 per cent. of the dry substance. These are contained in the *bone ash*, of which we shall speak later.

When a bone is treated with ether and petroleum to remove fat, and then soaked for some time in dilute hydrochloric acid, the mineral salts dissolve, and a skeleton of the animal matter is left of the original shape of the bone, but soft, elastic and semi-transparent. It is better to use acid of not more than 5 per cent., and to renew it occasionally, as a stronger acid and long contact is apt to rot the ossein, and is difficult to wash out. The phosphates can be precipitated from the solution by ammonia. After thorough washing,

the ossein is neutral, tasteless, and contains little ash; on drying, it becomes hard and somewhat brittle. Boiling with water of course converts it into gelatin, more rapidly in the presence of acid, but in this case gelatin-peptones, or "gelatones," which do not gelatinise, are liable to be formed.

It was formerly stated that collagen and gelatin had the same elementary composition, and that the change in properties was merely a physical one, similar to many cases of physical isomerism that are known in chemistry.

This idea is supported by the fact that the analyses of purified bone-cartilage, isinglass, and gelatine from connective tissue, after drying, give approximating results. They are calculated as free from ash.

	Collagen (Bone). Mulder.	Collagen (Isinglass). Mulder.	Collagen (Bone). Fremy.	Gelatin (Connective tissue). Chittenden.	Gelatin. Allen.
Carbon .	50·40	50·76	49·81	49·38	50·2
Hydrogen .	6·64	6·64	7·14	6·81	6·7
Nitrogen .	18·34	18·32	17·32	17·97	17·9
Sulphur . } Oxygen . }	24·64	24·69	25·67	0·71 } 25·13 }	25·0
	100·02	100·41	99·94	100·00	99·8

But the opinion now held is that the change is really a chemical one of *hydrolysis*, or combination with water, by which collagen is first converted into gelatin, then into *gelatoses* (analogous to the proteoses or albumoses derived from true proteids), next into gelatin-peptones or *gelatones* (similarly analogous to peptones from true proteids), finally into amido-acids, lysine, lysatine, etc.

Hofmeister considers gelatin as a definite hydrate of collagen, which is re-converted into the latter by heating to 130° C. This would explain the correspondence between the

analyses of the dried substances. He suggests the following formulæ and equations :—

$$\underset{\text{Collagen.}}{C_{102}H_{149}N_{31}O_{38}} + H_2O = \underset{\text{Gelatin.}}{C_{102}H_{151}N_{31}O_{39}}.$$

$$\underset{\text{Gelatin.}}{C_{102}H_{151}N_{31}O_{39}} + 2H_2O = \underset{\text{Semi-glutin.}}{C_{55}H_{85}N_{17}O_{22}} + \underset{\text{Hemicollin.}}{C_{47}H_{70}N_{14}O_{19}}.$$

The two latter bodies being gelatones, the first sparingly, the latter easily, soluble in 70 to 80 per cent. alcohol. He passes over the formation of gelatose.[1]

Gelatin.[2]—When pure, a hard glassy substance possessed of considerable elasticity, neutral and free from odour, taste, ~~or smell~~, swelling up but not dissolving in cold water, insoluble in strong alcohol, ether, hydrocarbons or oils. It is a typical member of the class of *colloids* (κολλα, glue), characterised by their gelatinous nature, non-diffusibility, and absence of crystallisation. Gelatin contains a small proportion of *sulphur*, which it has been argued is due to an impurity, as it varies in different samples, and is stated to be sometimes absent. Thus A. H. Allen quotes Schlieper as having found 0·12 to 0·14 per cent. in the products from bone and ivory, Von Bibra "always very appreciable quantities in bone gelatin," Hammarsten 0·7 per cent. in fine commercial samples yielding 1·74 per cent. of ash, while in his own

[1] The above formulæ are only *empirical*, and give no clue to the chemical structure. Schützenberger and Bourgeois propose $C_{76}H_{124}N_{24}O_{29}$ for the formula of gelatin : the former, from a study of the action of barium hydroxide, concludes that ossein is built up of three groups :—

1. A nitrogenous nucleus of urea or oxamide.
2. A series of acids $C_nH_{2n}N_2O_5$.
3. Fatty amido-acids $C_nH_{2n} + {}_1NO_2$, starting from amido-acetic acid or glycocine. It is certain that the latter group continually figure in its decompositions.

[2] It would be convenient that, when the *pure* substance is spoken of, the word should be spelt *gelatin*, as it is in most chemical treatises ; when the commercial article is meant the ordinary spelling *gelatine* should be retained. The word *glutin* is sometimes used, especially on the Continent, but is objectionable on account of the risk of confounding it with *gluten*, from cereals.

laboratory he found 0·17 per cent. in Nelson's, and 0·38 per cent. in Brazilian isinglass.

When heated, gelatin softens, swells and gradually darkens with an odour of burnt feathers, emitting alkaline fumes containing amylamine, $C_5H_{11}NH_2$, and other bodies, then burns with a sooty flame leaving a hard charcoal which slowly burns away to a white ash amounting to about 1½ per cent.

The changes effected by bacteria in gelatin and glue will be discussed in Chapter IV.

The most characteristic property both of gelatin and glue is the action of water. Gelatin and the higher grades of glue swell up in cold water without dissolving, absorbing up to ten times their weight, and forming a soft mass which liquefies completely on warming. In hot water all forms of gelatin dissolve; the solution, if weak, remains liquid on cooling, but, if stronger than 1 per cent., it sets to a jelly. The limit of gelatinisation perceptible at 0° C. is about 1 in 150. A jelly of 5 per cent. strength is firm even in summer. Particulars of water absorption, firmness of jelly, etc., will be given in Chapter V., on Testing. The solution rotates polarised light strongly to the left: the degree of rotation approximately ascertaining the strength.

PREPARATION OF PURE GELATIN.

If the swollen gelatin mentioned above be subjected for twenty-four hours to a stream of cold water, then washed four or five times with distilled water, the salts and many impurities diffuse out. The jelly is liquefied by heat, adding boiling water if necessary, filtered by pressure through a fine filter in a hot-water-jacketed funnel, and poured slowly, with agitation, into a large quantity of 90 per cent. alcohol. The gelatin is almost entirely precipitated in flocks which agglutinate and settle, the alcohol containing some gelatin, and extractive matters is de-

canted and recovered by distillation. The solution and precipitation is twice repeated, and the product washed with absolute alcohol and ether, dried in vacuo, finally by a heat not exceeding 40° C. It is then white, friable, and contains very little ash or sulphur.

Davidowsky prepares "pure glutin" from buckshorn by extracting the salts with hydrochloric acid, washing, removing the fat by lime water, boiling, and precipitating the liquefied jelly by alcohol. He states that "the coherence varies with the source".

Most varieties of *tannin* give with solutions of gelatin an almost insoluble curdy precipitate, which dries up to a hard, elastic, imputrescible mass. This reaction is connected with the production of leather; its chemical relations will be discussed in Chapter V. The other properties of gelatin will also be alluded to in subsequent sections.

Allen gives the following table of gelatin-producing substances and their congeners, which is valuable as showing what substances will *not* produce glue, as opposed to numerous patents which claim miscellaneous raw products as available for the manufacture:—

A. Collagens *or* Gelatoids.

Dissolved more or less easily by boiling water, the solutions gelatinising on cooling. Contain only a small quantity of sulphur.

1. *Collagen* or *ossein*, from bones, skin, etc.
2. *Chondrigen*, from permanent cartilages.
3. *Isinglass*, from fish bladders.
4. *Sericin*, from silk. On boiling silk with water under pressure it yields a yellowish transparent substance which gives a strong jelly, and resembles gelatin in being precipitated by alcohol or tannin, but is distinguished from

it by giving a precipitate by potassium ferro-cyanide. But waste silk is usually utilisable for other purposes.

B. Fibroids.

Elastin, from the elastic fibres left after the removal, by boiling, acids and alkalies, of the more soluble compounds of certain ligaments, especially the neck-band of the ox, *ligamentum nuchæ*. It often forms a residue of glue manufacture, removed in the settling, as it does not yield gelatin, nor dissolve without decomposition.

Fibroin is a similar insoluble substance obtained from silk and from spiders' webs.

C. Chitinoids.

Chitin, from the wing-cases of beetles, or the shells of crabs and lobsters, can be converted by strong acids into a gelatinous form, which, however, is of no utility.

Conchiolin, from shells of mollusca, is similar in properties, but differs in composition.

Spongin, from sponges, on boiling with water yields no gelatine.

D. Keratoids.

Keratin, from horns, hoofs, feathers, hair and wool, will be further alluded to in Chapter II.

Chondrin.

Certain materials, such as young bones while still in the soft state, and the "permanent" cartilages, such as those of the ribs and joints, consist mainly of a substance called "chondrinogen" or "chondrigen," related to ossein, and yielding, on boiling, a body named "chondrin," which resembles gelatine, but is weaker in gelatinising and adhesive properties, and is distinguished by a few differences in chemical behaviour.

It is prepared pure by boiling with water and precipitating with alcohol in a similar manner to gelatin, and then manifests like properties, except that its jelly has less

strength. Some recent researches tend to show that chondrin is a mixture of gelatin and mucin, but commercially the presence of the substance called chondrin, which is present in many glues, may be held to be detrimental; it is useful, however, for size. It is distinguished by giving, like mucin, a precipitate with acetic acid. For photographic work it is specially objected to, and may be tested for by adding a saturated solution of chrome alum to a 10 per cent. solution of the suspected gelatine in hot water, and well stirring, "when, if chondrin be contained in injurious quantity, the liquid will gelatinise while still hot". But, unless a precipitate is also given by acetic acid, this test cannot be considered conclusive. Most photographic gelatines contain but little chondrin.

Mucin.

This name includes a number of slimy bodies, present in many tissues, which swell up in water but do not really dissolve. They are soluble in lime water and soda, therefore are ordinarily removed with the liquors of liming. Salt not stronger than 10 per cent. dissolves them, but when more concentrated they are precipitated. They have no adhesive nor gelatinising power, and show a strong tendency towards "foaming," therefore their presence should be avoided in glue manufacture. The use of alkalies in some processes of treating is found to encourage foam in the glue produced, a fault that is also found more commonly in glues made from salted than from limed hides, two facts that seem to point to the hitherto unobserved presence of mucin. The addition of acetic acid will reveal the impurity by causing a precipitate in the liquor.[1] The mucins are also thrown down by alum, so would be removed with other things in this method of clarifying.

[1] The addition of a small quantity of acetic acid to the glue liquor might be tried as a remedy for foaming, afterwards straining or settling, and neutralising with soda, not chalk.

The statements are continually recurring that "gelatine is the purest form of glue," and that "glue is impure gelatine". There is no doubt that this is only partially true. Just as gelatin is a product of the action of heat and water on collagen, so glue is the result of the same action on gelatin, the hydrolysis being carried further. Brannt, following Davidowsky, holds that "glue is the product of several transformations:—

"I. *In drying the hide.* Because the result of boiling green hide, prepared in the usual manner by liming, etc., but not dried, will be an entirely different product of less consistency than that obtained by drying the hide after liming and then boiling.

"II. *In boiling.*

"III. *In drying the obtained jelly.* This may explain the fact that the jelly, which is not yet converted into glue, differs in its behaviour from glue solution.

"IV. It is well known that when boiled for some time glue does not gelatinise. We distinguish therefore:—

"(*a*) Glue-yielding substance.

"(*b*) Crude glue.

"(*c*) Jelly.

"(*d*) Glue.

"We believe that, by reason of our experience, we are justified in making this distinction between glue-yielding substance and crude glue. Lime carefully, *e.g.*, fresh calves' heads, such as the tanner cuts off after raising the skin, and then boil them without previous drying—the result will be a turbid soup, containing, though everything be dissolved, no jelly whatever, or at least very little.

"(*b*) *Crude glue* is glue-yielding substance freed from foreign matter, and *physically prepared by drying.*

"(*c*) *Jelly.* Its adhesive power is far less than that of solution of finished glue, and it will become more quickly

putrid than the latter," because (1) it contains more water; (2) it is not so completely sterilised; (3) it does not contain the empyreumatic substances of glue which are antagonistic to bacteria. "At 21° C. a 'jelly' putrifies under twenty-four hours, while glue solution can be kept much longer."

To render clearer the practical differences between glue and gelatin, I instituted the following experiments:—

A 5 per cent. and a 50 per cent.[1] solution of (*a*) "Coignet's gold medal" gelatine in thin transparent sheets, and (*b*) a dark Scotch glue of average quality, were prepared by heating carefully with water to 70° C. in wide-mouthed stoppered bottles, and stirring so as to dissolve as soon as possible. The tenacity of the stronger solutions was determined between stone-china blocks as described in Chapter V., while the consistency of the jelly at 0° C. and the viscosity of the liquid at 25° C. were ascertained in the 5 per cent. solutions. The results were tabulated:—

	Strength per cent.	Characters.		Tenacity—Breaking weight: lb. per sq. inch.		Consistency of jelly at 0° C.	Viscosity at 25° C., seconds required.
		Liquid.	Jelly.	20 hrs.	48 hrs.	Units.	
Gelatine	50	Inodorous, tasteless, neutral, imperfectly liquefied.	Pale, tough, opalescent.	159	446	...	...
Glue .	50	Strong odour, very viscid, slightly alkaline.	Dark brown, hard, rather cloudy.	172	480	...	...
Gelatine	5	Like the 50 per cent.	Nearly clear, stiff jelly.	...	...	12,555	40
Glue .	5	Like the 50 per cent.	Liquid at summer temperature, a weak jelly at 0° C.	...	...	1218	25

[1] There is often some confusion in stating the strength of glue solutions, three distinct methods of making up a nominally 5 per cent. solution being used: (1) 5 grammes glue *plus* 100 cc. water; (2) 5 grammes in 100 cc. of the

The "units" of consistency require some explanation. The 5 per cent. liquids (*a*) and (*b*) being reduced to 0° C. by a bath of ice and water, a glass tube 13 millimetres diameter was supported vertically, so as to move easily between guides, its lower closed and rounded end resting on the jelly. It was then weighted with shot (in later experiments with mercury) till it began to descend steadily, and the weight of shot plus tube ascertained. The figures were:—

(*a*) 232·5 grammes sank 50 millimetres in 270 seconds.
(*b*) 20·3 ,, ,, ,, ,, 300 ,,

$$(a)\ \frac{232{\cdot}5 \times 270}{5 \text{ centimetres}} = 12{,}555 \text{ units.}$$

$$(b)\ \frac{20{\cdot}3 \times 300}{5} = 1{,}218 \text{ ,,}$$

(See Chapter V., p. 122.)

As the 50 per cent. gelatine, when hot, was of such a consistence that it was nearly impossible to work with, continually forming skins, and giving too thick a layer between the blocks, a weaker solution of each substance was tried for tenacity.

Breaking strain of 33 per cent. solutions of glue and gelatine, mounted between blocks of old mahogany, area of surfaces 1 square inch, compressed by a weight of 4 lb., for forty-eight hours at 23° C. in a dry room.

Gelatine	550 lb.
Glue	610 lb.

To ascertain the action of heat on the solutions:—

Experiment 1. *With concentration.* 100 cc. of the 5 per cent. liquids were evaporated down in a water bath at 95° C. till 10 cc. was left: the solutions were now of 50 per cent. strength. The formation of a skin was avoided by occasional agitation. The gelatine, owing to

made solution; (3) 5 grammes in 100 *grammes* of solution. The method of preparation being ofter omitted, the results of published experiments are not strictly comparable. In these experiments method (2) has been adopted as more convenient. Evaporation in all cases must be avoided.

its viscidity, required a much longer time to evaporate—twelve hours, as against five for the glue. Cooled to room temperature (22° C.), the gelatine set, but was much less firm than the original 50 per cent. solution, while the glue was simply a slimy liquid. The tenacity was again tried as above. The results were: gelatine 602, glue 184 lb. Therefore, the heating had slightly improved the tenacity of the gelatine, but reduced that of the glue.

Experiment 2. *Without concentration.* Two quantities of 300 cubic centimetres of glue and gelatine were heated in closed bottles for seventy-two hours continuously to 100° C., then left for forty-eight hours at room temperature. Both were now quite liquid, and remained so even at 0° C., therefore the gelatinising property had entirely disappeared. In the glue the smell had become intensified; the gelatine remained clear, but had acquired a yellow-brown colour and a gluey odour. The viscosities were: gelatine, 13; glue, 13·5.

A chemical examination was also made of the two liquids. As the bottles had been carefully sealed, the total nitrogen would be the same as before the heating. Distilled with alkaline permanganate, they gave the same amount of ammonia before and after heating.

To ascertain whether the liquefaction affected by heat was of the same character as that caused by enzymes, whether from digestion or bacteria, the solution of gelatine was treated with ammonium sulphate, which throws down gelatin and gelatose, but not peptones or gelatones. The precipitate was nearly the same in amount as that obtained from fresh commercial gelatines, whereas after artificial digestion or bacteriolysis the precipitate would be much less. The conclusions drawn from these researches are :—

1. That gelatine and glue are distinct substances, the latter formed from the former by heat and evaporation.

2. That the action of heat is different from the peptonisation caused by digestion or bacteria.

3. That gelatine in turning into glue loses gelatinising power, becomes more liquid, and somewhat increases in adhesiveness.

4. That after about twelve hours' heating all the prominent physical properties of value decline, while the chemical reactions are little altered.

Hence it might be possible to restore the qualities of a glue which had been spoilt by heating. With this view the effect of formaldehyde, which in small quantity is known to increase the stiffness of jelly, was tried. The liquid resulting from the seventy-two hours' heating gave, on evaporation, a hard, transparent, brittle residue, easily soluble in ice-cold water, and almost destitute of adhesive power, therefore not gelatine. Addition of 1 in 2000 formaldehyde did not precipitate the liquid, but after the evaporation left an opaque brittle residue, almost insoluble, and not adhesive. No restoration seemed to have been effected in this way.

The " souring " of glue liquors is due to bacterial action. Some notes on the point will be found in Chapter IV.

Classification of Glues.

The chief commercial varieties of gelatine or glue can be roughly divided into two groups, subdivided again by the source from which they are derived :—

I. *Glues proper.*—Varieties chiefly used for their adhesiveness and tenacity :—

(*a*) Skin, hide, or leather glue.

(*b*) Bone glue.

(*c*) Fish glue.

II. *Gelatines.*—Those used principally for their gelatinising properties, and differing from ordinary glue in their purity and freedom from colour and odour. They are also

used for filling, clarifying, glazing and stiffening, and for all purposes where whiteness, transparency, and absence of colour, odour, and taste are demanded. They are all obtained, like glues, by the action of heated water, sometimes assisted by dilute acids, on materials of special selection.

(*d*) Skin gelatine, from carefully cleaned and treated intercellular connective tissue, such as skin, tendons, ears, intestines, or even the sheaths of muscular fibre.

(*e*) Bone gelatine. Crushed bones yield about one-third of their weight of an excellent gelatine if exposed on trays or gauze, in a closed steam-jacketed vessel, to a regulated descending flow of water, and an ascending current of moderately superheated steam, when the earthy salts remain undissolved, and a nearly clear solution of gelatine is obtained. These materials, (*d*) and (*e*), if carefully prepared, are practically equal to the next, they are alike in composition, but would be regarded as a "substitute," or even as an adulteration, if supplied in place of the following varieties :—

(*f*) Fish gelatine, from the bones, skins, and swimming bladders of fish.

(*g*) Isinglass, the most expensive variety, derived from the swimming bladder of the sturgeon.

In addition to these are several varieties of more or less importance :—

(*h*) Liquid glues.

(*i*) Soluble and mouth glues.

(*j*) Vegetable glues, "artificial glues," or glue substitutes.

III. *Size.*—Prepared already in the moist or gelatinous state from light-coloured glues or from gelatines by treatment with hot water.

Grades of Glue.

Besides these broadly distinguished commercial forms, the trade recognises a large number of qualities known as

grades, and separated not always by their value as regards physical properties of colour, tenacity, etc., but often by their fitness for special purposes. The price, like that of other commercial products, is frequently artificial. It is often less necessary to prepare a glue that shall possess ideal qualities as regards appearance or tests, than to suit the fancy of a customer. It has been found even that a glue which will give excellent results with one consumer may fail with another for the same purpose, on account of some slight difference of working. Therefore, it has been customary to keep a book with a record of each important client's special requirements, the test figures and characters of the article he prefers, and memoranda of the details in the process that has obtained it. After a time this becomes simplified by the storage of numbered standard specimens, recording particular *grades*, each of which can be immediately referred to the date and particulars of manufacture as recorded in the firm's books. By this means it is secured that future supplies shall be always "up to sample," which is often a matter of contract. Exact and regular working, strict cleanliness, observance of temperature and other physical data, and scientific supervision, are clearly necessary. "Rule of thumb" is never quite certain to produce the same article twice.

It is often said that the variation in raw materials will occasion fluctuations in the quality of the product; this to a certain extent in ordinary working is true; but with substances such as glue, which depend for their essential properties on a chemical entity of practically definite composition like gelatine, there is no reason why the process should not attain almost the exactness of a chemical analysis, where the sample is accurately averaged, weighed quantities are taken, and conditions of temperature, strength and time are rigidly observed.

On a large scale the raw materials, judiciously chosen,

will average themselves, and then, if at every point the conditions are kept intelligently constant, the *quantity* of the finished product may vary, but its *quality* should be certain, the price being effected by the yield.

Hide glue has the strongest adhesive power, and also the highest price; it is mainly employed by carpenters and joiners. The best grade of hide glue is used by cabinet-makers; it must have "great body and light colour, must not be too quick in drying, or the joint may crack, nor too slow, or the work will be delayed; it must be sweet, and not turn dark over night". The workshop test is simply that of joining two pieces of wood in different ways, and after allowing time to set, generally forty-eight hours, trying the joint by hand, as there is rarely a testing machine or weights available. (See the section on Machine Testing, Chapter V.) The result will obviously depend entirely on the skill and judgment of the manipulator, and the fairness with which the experimental joint is made. In America maple is generally used; in England, mahogany—this should not be new or unseasoned.

For *Veneers* the "foam test" (*q.v.*) is of great importance, and is usually the first property inquired into. It is well known that the strength and soundness of a joint is much impaired in all cases by the presence of air bubbles. In veneering the glue must not foam when applied with revolving brushes. "Veneers glued with such stuff do not stick; they split off—and if they do not come off altogether, they show a rough surface full of air bubbles." The remark as to one operator getting a good result with a glue which does not suit another particularly applies here, as the fault frequently lies with the strength used, or the rapidity of working, rather than with the quality of the glue.

We shall speak elsewhere of the practice of incorporat-

ing more or less inert powders with the glue in the course of manufacture, usually at the end of the boiling, resulting in the production of an opaque whitish product. The "barytes" (sulphate of barium), used in some varieties of "Russian glue," is purified from iron, etc., by treatment with hydrochloric acid, then ground, carefully levigated in water, and mixed by stirrers with the melted glue. If not finely divided it is apt to settle, on account of its weight; the same is the case with *white lead*, which is also used.

Russian glues may contain 4 to 8 per cent. of barium sulphate, white lead, zinc oxide, or chalk. They are met with in dirty white short thick cakes. The heavy powders add to the weight of the product, "without injury to their adhesive power," according to some authorities, "with a distinct increase," according to others. Experimental tests have shown, as was at first probable, that of the variety of powders tested, the effect in small quantity was either *nil* or a slight decrease; in large quantities the product was distinctly weaker; in none was there any augmentation of strength. They are manufactured to answer the demand in certain quarters of the trade, and also more especially to keep a certain brand distinct. In the States they are included under "Coloured Glues," and usually contain oxide of zinc, which addition prevents souring, but is apt to cause foaming when used with rotary brushes.

Commercial glues are usually opalescent, or even may be "muddy," turbid, or very dark brown, like some Scotch glues, without inferiority of strength. A dark glue, when the colour proceeds from the materials, and not from overheating, will often be stronger than a paler glue which has been chemically bleached. Still, for the superior classes of work a glue of clear amber, or at most brown-yellow colour, is required. It should be free from streaks or spots,

which show imperfections in the manufacture, dry and hard, with a glassy fracture, not too brittle, but somewhat elastic.

Cologne glue is found in short thick cakes, very pale in colour, but of good strength if properly prepared. It is made from scrap hide, or even from some kinds of offal, limed, and then cautiously bleached by a solution of chloride of lime, using about ½ lb. per cwt. The process is carefully watched, and is stopped when the desired effect is produced, as if kept on too long the stock would be rotted and the product spoilt. Thorough washing is necessary afterwards, and sometimes the use of sulphite of sodium as an "antichlor" to remove any remains of hypochlorite. Some manufacturers, after soaking half an hour, add enough hydrochloric acid "to give an acid taste," allow to act for a quarter of an hour, and wash.

Russian glue is a trade name indicating the particular kind of opaque article we have described above. It may be skin glue or bone glue. Clear glues are also made in Russia, the raw material being abundant. A very large quantity of horse hides is disposed of, with corresponding clippings and offal, in the Nijnii Novgorod market, with also sheep and goat skins from Siberia.

"*Patent glue*" is a title applying to an indefinite number of preparations, but specially means a good bone glue, in thick cakes of a deep dark brown colour, not showing net marks. It is very glossy and swells up much in water.

"*French glues*" (the word not always implying that they have been made in France) are light-coloured thinnish square cakes; they have been chemically bleached, usually with chloride of lime, but in the joinery trade are often found stronger and better for work than very dark reputed "Scotch glues" of uncertain character.

"*Gilder's glue*" occurs in very pale yellow thin cakes,

tied in packages of 1 kilogramme. It is skin glue bleached with chloride of lime, and is only the first runnings from the boiler. It is often difficult to dissolve.

Size glue and *parchment glue* are also trade names; the latter was once almost exclusively used in bookbinding.

"*Paris glue*," used for sizing, is brown, opaque, and almost always soft, and is employed by hatters. It is intentionally too long boiled, so as to be hygrometric and hardly adhesive.

Fish glue from the skins, bones and swimming bladders, is much used by cabinetmakers, and is said by Wagner, when properly made, to be indistinguishable from glue made from bones and other animal refuse.

CHAPTER II.

RAW MATERIALS AND MANUFACTURE.

As to the sources of *skin glue* the following information has been given :—

Calf and sheep skins yield a superior glue : that from horse hides is usually dark and poor in quality, although with careful working a strong product can be obtained from the latter.

Tannery waste, *i.e.*, the foot, head and buttock cut off before tanning, may give 44 to 46 per cent. of glue. Scarf skin of bullocks' hides and waste in fleshing the hide, tendons and hinder parts of cattle yield from 30 to 35 per cent. ; horse sinews 15 to 18.

Bullock's feet and parchment shavings are the richest stock, giving 62 per cent. of their weight of glue. Among other materials are :—

Old gloves, rabbit skins from which the hair has been removed by hatters, dog and cat skins, earlaps of sheep and cows, sheep's feet with the tendons and small bones, waste of skins generally : these may yield 38 to 43 per cent. Refuse of tanning and of kid gloves forms a light product, and requires no preparation.

Skins of hogs, hares and rabbits yield a light-coloured glue of little consistency, used for sizing and paper. Pig glue is largely made in Chicago.

A considerable number of skins come to the warehouses which have been used for packing various articles, such, for

instance, as indigo from South Africa: they have been so knocked about in transit that they are useless for tanning, but they will frequently yield 50 to 55 per cent. glue. Waste of Buenos Ayres skins may give 60 per cent.

Cartilages and other waste of fish are usually made into gelatine or imitation isinglass.

Good stock should yield 50 per cent. glue. Poor may be as low as 20 per cent. Stock before drying is said to be "green," and is stored during the winter in wooden vats or in cemented brick tanks filled with lime water about half saturated and covered up from the air. As to judging of glue stock, some valuable notes are given in a work on glue lately published by the American Provision Company, Chicago.

"Dry uncured or salted stock, such as raw hide or South American, if soaked for twelve hours in cold water gains about 50 per cent. in weight, and still remains tough, and the water sweet. The moisture, dirt and salt should not be over 10 per cent.

"Green salted stock, such as hide pieces, sinews, calf heads and pates should have no excess of salt, nor be foul, discoloured, or heated; should be tough, with the hair not loose, and have a mild animal odour. Moisture and salt not over 40 per cent.

"Dry limed stock soaked twelve hours develops a characteristic odour, and should be firm, fibrous, and have no slimy pieces. The water should not be dark. Lime, sand and dirt not over 5 per cent.

"Green limed stock should be smooth and soft, any remaining hair being easily detachable, while the liquor should be fairly clean, sweet, and not too alkaline.

"A large quantity of waste bones are accumulated in the preparation of tinned provisions; if these have not been overheated, and are in good condition, a considerable amount of glue can be obtained from them, the bones of the head,

ribs, and feet giving a better yield than those of the thighs and legs.

"Horn piths should not contain over 12 per cent. moisture, and should not have been overheated in drying; they should have been cleansed from skin and hair, which are of little value to the glue maker.

"The age of the animals yielding glue stock has an important influence on the product. While from younger animals the product, as a rule, is of lighter colour, more abundant, and more easily obtained, it contains more chondrin, so, that for solutions of equal strengths, those from mature animals will be found to be of the greater consistence and the glue more solid.

"Abroad, dry hides are often, for weighing, soaked in 'chlobarium,' a solution of barium chloride, and then in a bath of dilute sulphuric acid, 1½ per cent., which readily soaks in, combines with the barium to form the white insoluble powder of barium sulphate, leaving weak hydrochloric acid in the fibre, to be afterwards neutralised in liming, the chloride of calcium dissolving out. This treatment affects considerably the subsequent making of glue, as, besides the effects of the acid, the sulphate of barium will render the liquors cloudy, and be difficult to clarify. Of course if 'coloured' glues are to be made this will be no detriment."

Skins are composed of a number of elements of which the most important are:—

1. Scarf skin or *epidermis*. Thin, horny, and mainly composed of *keratin*. It is scraped off before tanning, and does not enter into the preparation of glue. It carries the hairs, accompanied by fat and sweat glands.

2. The *corium* or true skin, chiefly composed of interlacing white fibres of connective tissue (95 per cent.) embedded in a structureless matrix of *coriin*. In the operation of liming, the coriin is in part dissolved and the fibres loosened,

hence the softening effect, which should not be allowed to proceed too far, or waste will be occasioned. Under the action of hot water the corium is gradually but entirely dissolved, and converted into gelatine—only the hairs, glands, vessels, nerves, muscular fibres and a little yellow elastic tissue are left, and form a small quantity of sediment. The microscopic examination of glue stock is often of great value. It is conducted by soaking for some days in alcohol, and cutting very thin sections with a razor; these are examined under the microscope with and without staining, or soaking in glacial acetic acid and glycerine.

Keratin is the nitrogenous horny substance constituting hair, epidermis, horns, hoofs, feathers and nails. It is very difficult to dissolve in either hot water or acids, but on protracted heating it gives a solution which does not gelatinise; consequently the forms of keratin possess no value for glue making, and have to be removed as far as possible. They are generally used up in the manufacture of ferrocyanide of potassium (yellow prussiate), in the manure or other trades, among which may be mentioned the use of a large quantity of hair in plastering, and of horns and hoofs for handles, etc.

It has been asserted that the bones, and other parts of birds and reptiles, yield a superior gelatine. I have not found commercial confirmation; moreover, the supply would be small.

Bones contain about one-third of their weight of animal matter, which is almost entirely convertible into glue. The soft bones of the head, shoulders, ribs, legs and breast, and especially deer's horns, and the bony core of the horns of horned cattle, yield a larger quantity of glue than the hard thigh bones and the thick parts of the vertebræ, which are principally composed of calcium phosphate, and require a more prolonged treatment to extract the glue-making constituents. *Buckshorn*, the osseous nucleus, is reckoned a

superior stock: it contains very little fat, and requires no steaming before liming.

The upper thigh bones are used for making piano keys, handles, etc., while hoofs and horns are separated, as they yield no glue (see Keratin), and are used for other purposes.

Fish glue, from the skins and bones of fish, has very little colour and generally less tenacity than hide or bone. It always retains a fishy odour, but is preferred for making some cements and liquid glues, and for other commercial purposes. Sole skins are much used. Carefully deodorised by a small quantity of chlorine, and decolorised by animal charcoal, fish offal is made into gelatine or imitation isinglass.

So-called glues are prepared from various proteid substances; in Chapter IV. a few of them are described.

Vegetable matters have also been used, principally those containing pectin or vegetable jelly. Under the name of "Vegetable glue," Frank Hepburn has patented a glue or sizing obtained from the palmetto or similar plants. It consists largely of pectinous matter. The roots or underground stems are disintegrated and steamed at 300° F. for an hour, then boiled with water. The liquid is clarified and evaporated *in vacuo* to the required density. It is said to possess considerable viscosity, to be tenacious, and when set, to be little affected by damp or liquids.

Various gelatinous bodies derived from seaweeds will be described in Chapter IV.

Liming.

The preliminary liming process often constitutes a business quite separate from that of the glue boiler, so that the stock is purified before being sent to the glue manufacturer, who again, however, treats it with weak milk of lime followed by thorough washing previous to boiling. Bones are sometimes steamed for a few hours to soften

them before liming. Foot-bones and buckshorn are not steamed: they are left in the lime vat eight to fourteen days.

Besides the "collagen," or matter that in boiling yields gelatine or glue, there are a number of other substances present in the heterogeneous mixture known as "glue stock". Even, after removal of fat by steaming, ethereal solvents or alkalies, only a portion of the residue is convertible into glue. In the dermis at the back of the scarf skin a quantity of mucin is frequently found; this is soluble in dilute alkalies, and possesses no gelatinising power. The same is the case with the remaining blood, gummy and extractive matters, which would darken the colour and convey no strength, besides increasing the tendency to putrefactive change. To dissolve these, at the same time softening and loosening the tissue, is the object of soaking in lime water or "liming". If the fat has not been previously removed, it also is acted on more or less rapidly by the lime, being "saponified" or converted into calcium salts of the fatty acids, so-called lime soaps, which generally detach themselves, and float as a curdy scum on the soak.

Careless liming will produce a fat running high in free fatty acids, which means for each 13 per cent. of free fatty acids a loss of 1 per cent. grease on account of the liberated glycerine. The safest way to prevent loss of fat is to trim the stock carefully of all fatty tissue, and to render such trimmings separately.

The liming and drying are generally carried out in the tanyard. If not carefully done by the tanner, the stock is of little value to the glue manufacturer. If the stock lies too long in a heap, especially in summer, it becomes putrid, and the value is not restored by liming. On the other hand, it has been stated that it is sometimes advantageous to allow the offal to become somewhat decomposed, and then to disinfect with chlorine or sulphurous acid, the idea being

that extraneous matters are more easily removed. Such a proceeding is very dangerous. If badly dried after liming, the stock becomes mouldy. Drying in the open air is rarely practised, and then only in the spring and autumn, as, if the stock is allowed to freeze, it appears that the fibre is so injured that it yields glue of very little consistency (Brannt); in the summer the stock is liable to putrefaction. During liming the hair is loosened, and is afterwards easily scraped off. Rotary vessels save considerable time and render the process more regular. The proportion of lime liquor to stock should be such in ordinary vats that there is room for stirring and circulation. It is better to have excess of liquid than too much solid material. It has been remarked elsewhere that the liquid of the liming vats should not become very dark coloured, ammoniacal or putrid; each of these faults indicating a loss of glue substance, and a deterioration of the product. An American authority asserts that "every pound of ammonia escaping is equivalent to twenty pounds of glue stock lost". This is probably an overstatement, but the actual ratio of ammonia to dry gelatine is about 1 to 6, so that a large loss, both in quantity and quality, occurs if the liming be not properly conducted. A great part of the care that is necessary is to control the action of the innumerable bacteria—mostly micrococci—which may obtain access to the liming liquid. The lime itself acts as a mild antiseptic. Pettenkofer held that it "destroyed rapidly and completely the organisms of putrefaction," but we now know that it simply modifies, differentiates, or retards their action. The well-known use of lime water for preserving eggs depends on the deposition of carbonate of lime in the pores of the shell, rendering it impervious, and also on the lime coagulating the albuminous envelope of the egg. In the same way, in the liming vat, the surface of the liquid becomes continually coated over, by the action

of the carbonic acid of the air, with a film of carbonate of lime which is fairly coherent, as shown by touching it; and the air, and particularly the bacteria, are thereby to a great extent excluded. The lime coating on the pieces themselves is also a protective.

Stock, which has become soft or discoloured, may sometimes be restored by steeping for twenty-four hours in clean water, washing, again soaking in lime water for some days, washing again, draining, and drying at a moderate heat.

As slaked lime, or calcium hydrate, is so slightly soluble in water—1 part requiring 700 parts for solution—it is customary to employ "milk of lime," or lime suspended in water, for the first soaking, and lime water or solution of lime for the subsequent ones. Many samples of so-called milk of lime that we have examined have been quite valueless, having become carbonated, or a bad quality of quicklime having been originally employed. It must be remembered that only the *hydrate* of lime which is present in solution in lime water is of use, whereas in "milk of lime" so much carbonate and other impurities may be present that the liquid, though thick, may be quite useless. The value of a lime should always be tested by determining the amount of real calcium hydroxide, $Ca(OH)_2$, contained in it. The operation is an easy one, and is thus conducted: Water, free from carbonic acid, is first prepared by boiling distilled water for half an hour in a strong round-bottomed Bohemian or Jena flask. While steam is still issuing, the flask is removed for an instant, closed by a well-fitting greased cork or a caoutchouc stopper, and allowed to cool. When the temperature has somewhat fallen, the cooling may be cautiously accelerated by dipping into a pail of warm water, then transferring to the cold stream from a tap. The water may be preserved in the flask, or, preferably, a number of bottles with vaselined stoppers should be filled *quite full* and retained for use.

From the sample of lime, well mixed, a small portion (about 0·25 gramme) should be accurately and rapidly weighed, placed in a wide-mouthed stoppered bottle holding about 300 cubic centimetres, 250 cc. of the boiled water added, and the whole vigorously shaken at intervals for one hour, and then allowed to settle. The whole of the calcium hydrate will now have dissolved. Fifty cc. of the clear liquid should now be withdrawn by a pipette, transferred to a flask, coloured with an indicator (either phenol-phthalein, methyl-orange or litmus may be used), and its alkalinity determined by running in decinormal hydrochloric or sulphuric acid from a burette till the change of colour occurs. Each cubic centimetre of the acid corresponds to ·0028 gramme of calcium oxide, or ·0037 gramme of the hydrate, $Ca(OH)_2$. The amount by calculation will give the percentage of real lime present in the sample. It is well to notice that any soda or potash present will equally neutralise the acid, and be returned as lime, but as these are of almost equal efficiency their presence *in small quantity* has no disadvantage. For special work it will be necessary to have a full analysis. As a rule the product made from limestone, or "stone lime," is the best article in commerce, and is much more free from stones and clay than "grey lime" or "shell lime". The best stone lime contains sometimes only ½ per cent. of impurities, and seldom more than 5 per cent., while inferior kinds of grey lime may contain as much as 50 per cent., and would be of little use in glue making.

A good sample of quicklime having been obtained, it is slaked, and the powder of calcium hydrate removed without delay to closed wooden mixing vats, where it is stirred by mechanical agitators with the requisite quantity of a soft water. It is a great mistake to use too much lime: the strength in real lime should be 1 to 2 per cent. of $Ca(OH)_2$, and can be calculated from the result of the alkalinity test.

Thus, if the content of calcium hydrate have been found to be 90 per cent., it will be necessary to use 11 parts of the crude lime to 1,000 parts of *distilled* water, or 770 grains per gallon. But as soft, or softened, water, containing some carbonic acid and carbonate, and therefore occasioning a certain amount of waste, must for economy be employed, it may be laid down that about two ounces of good lime per gallon will yield a milk of lime of sufficient strength. It should always be thoroughly mixed, and strained from lumps, as these occasion spots in the stock, with subsequent faults in the glue, and waste of acid if the sulphurous process be used. The practice of commencing with a weaker milk of lime, and increasing the strength for the second and third soakings, although adopted in a number of works, particularly in America, is not so good as that of treating first with lime milk properly prepared in the way we have recommended, and then with clear lime water of maximum strength.

Both milk of lime and lime water must be protected from the air. The latter should be clear and colourless, and its strength should be periodically tested as above. It is obvious, however, that a saturated lime water can always be decanted from a milk-of-lime vat that has been stirred and allowed to settle. The solubility of lime at various temperatures is given as follows in grains per gallon:—

Temp. C.	Temp. F.	Grns. CaO.	Grns. $Ca(OH)_2$.
0°	32°	80	106
15·5°	60°	70	92·8
100°	212°	40·5	53·6

the solubility decreasing as the temperature rises.

Filter Presses for Extraction, Washing, and Clarifying.

For nearly all purposes where an insoluble precipitate has to be separated from a liquid, or a liquid has to be made clear, the old-fashioned process of sedimentation in vats and

decantation of the liquor has been replaced wherever possible by the use of filter presses (Fig. 1) for the following reasons:—

1. In many cases, when the precipitates are light and flocculent and easily raised by vibration, convection currents or entangled bubbles of air, the process of deposition takes a considerable time, during which a great amount of floor room and plant is monopolised. Some precipitates absolutely refuse to settle clear within a reasonable time without the use of heat or of a clarifying agent, involving additional expense; although the precipitate be naturally heavy, it is so finely divided as to be intractable, like the familiar case of sulphate of barium.

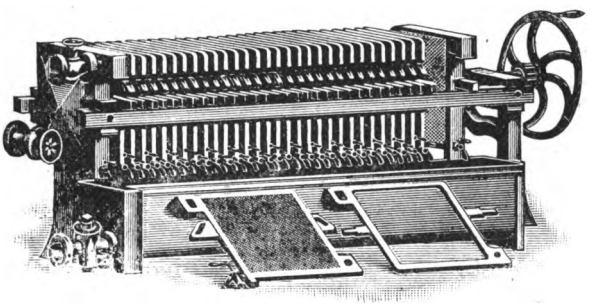

Fig. 1. Filter Press.

2. During the time required, detrimental changes are apt to arise in the liquid, even when carefully protected, or if (at further expense) a preservative like borax or salicylic acid be used. This is particularly the case in the glue trade.

3. It is impossible to draw off more than a varying fraction of the liquid from the precipitate, a proportion depending on the care devoted to the operation, and to the nature of the precipitate, and circumstances connected with quietness, density and temperature. The residue is a sludge of precipitate and liquid; the option of further treatment being decided according to the value of the materials between.

(*a*) *Washing by decantation;* that is, flushing with further quantities of water, mixing, subsidence, and syphoning or tapping off as before; this would require to be repeated several times, and the washing would never be complete. A very large volume of wash water is also required.

(*b*) *Discharging,* if the mixture will not pay for further treatment; with the accompanying difficulties of disposal owing to odours, river pollution, etc., besides the waste of material.

(*c*) *Drying by heat or burning,* with a consumption of fuel corresponding to the amount of water remaining, and the same waste of matter.

On the other hand a filter-press can, except in very rare cases, produce a clear liquid and a nearly solid cake with considerable rapidity, under a pressure varying with the character of the work, and with a great economy of space. The liquid is ready for an immediate continuation of the process in hand, while the cake can be either soft-pressed and washed, or if valueless, hard-pressed and dealt with further in the ways indicated above, with an extra facility as containing less water. It may be remarked that with the many modern improvements in saving waste products, it is very seldom that residues do not admit of being worked up to some advantage.

Filter presses are usually constructed with an iron framework on account of the greater strength. But where, as in the preparation of the better classes of size, or of gelatine, there is danger that accidental rusting or action of acids on the iron might occasion spots or general discoloration, filter presses of *wood* are available, and have been of late greatly improved. It is absolutely necessary that the wood should be well seasoned. When first used, even the best woods give off more or less tannin in washing and cleansing, so that the press is not really up to perfect efficiency till this has been extracted and washed out; then the press should

not be allowed to rest idle and dry, or it may crack or warp, nor to remain in contact with foul water, so as to develop moulds, green algæ, or offensive bacteria, which may each of them, in subsequent working, cause faults in the glue. A press, particularly a wooden one, should always be kept scrupulously clean ; if it is absolutely necessary for the wood to remain at rest for a time, it must be washed with dilute chlorine water, or very weak chloride of lime, then with clean good water and allowed to dry, but it is rare for a leak not to occur on resuming working. The filter chambers are now made recessed from a solid slab, and hence more durable than framed plates.

Water Supply.

In glue making, as in other manufactures, one of the first necessities is to have at command an abundant and regular supply of water. When starting a new factory in the colonies, where great facilities for economic production of glue often occur, owing to the cheapness and abundance of the raw material—which is often a by-product, though an important one, of the production of hides; hair, horn, and meat, either frozen or canned—failure has frequently resulted from a surprising inattention to this first requisite. The main features to be considered are :—

1. *Abundance and constancy of the supply.*—A very large quantity of water is wanted, even in a small factory, for the liquors, boilers, and especially for cleansing and washing. If this last item is stinted, the factory, as a whole, is apt to get " sour " or " foul," owing to the inroads of bacteria and moulds, and it will become almost impossible to turn out a good or marketable article. Therefore, the rainfall of the district must be taken into account, as if very irregular, storage in reservoirs will be necessary.

2. *Quality.*—The water of rivers is often plentiful and

soft, but turbid, discoloured, and organically contaminated. That of wells is frequently clear and colourless, but unduly hard. Rain water is very soft, but can rarely be collected in sufficient quantities. A good water for manufacturing purposes should be reasonably *soft—i.e.*, free from lime and magnesia salts beyond about 10 to 15 grains per gallon = 14 to 20 parts per 100,000—not containing an excessive amount of mineral salts, especially carbonate of soda, free from iron, also from sulphuretted hydrogen or more than traces of free ammonia. The presence of salt (chloride of sodium) is considered objectionable in glue making, as it has a liquefying quality.

The waste occasioned by hard water for boiler feeds is common to all manufactures. The effect of the deposit known as "scale" has been variously stated, but is always large. Approximately, the loss of heat increases as the square of the thickness of coating, thus if $\frac{1}{16}$ inch scale causes a waste of $\frac{1}{3}$, a hard scale $\frac{1}{8}$ inch thick will result in a loss of nearly 50 per cent.

For liming and cooking, the permanent hardness due to chlorides and sulphates of lime and magnesia does not interfere so much with the glue processes, as these earthy salts are not deposited on boiling. For this reason it has actually been proposed that water with very high temporary hardness, due to earthy bicarbonates, should be "acidified"—better "neutralised"—with sulphuric or hydrochloric acid to turn the carbonates into chlorides or sulphates. But excess of these salts, particularly of chloride and sulphate of magnesium, fixes the earthy base in the fibre of the stock, occasioning "pasting up," with a loss of solubility to the gelatigenous matter.

Failing a proper supply the chance of remunerative working will be diminished. Difficulties, however, may often be averted by—

1. Artificial softening, as in Clark's, the Atkins, Wright's or Archbutt-Deeley process (*vide Water Purification*, Rideal, 1897, Chapter X., "The Softening of Water").

2. Sand filtration, or such apparatus as the Hyatt, National, or other filters, which are worked by pressure and are much used in the States. It is always advisable to have periodic analyses made of the water.

Washing Limed Stock.

The excess of lime, salts, and dirt, must be thoroughly removed by repeated washing with water. As it is wasteful and injurious to unduly protract this process, it is necessary to test at intervals the liquors coming away. As soon as the impurities have been removed, the wash waters will be colourless, neutral, and on evaporating about 20 cc. on a water bath, will leave only the natural water residue, not blackening nor giving an animal odour on burning. The simplest plan is to place the limed stock in nets or wicker baskets suspended in running water, but this elementary method is open to several disadvantages :—

1. It fouls a large volume of water, and may lead to legal interference.

2. The very simplicity is apt to lead to neglect of precautions such as brushing away solid particles of lime or softened animal matters.

3. It is not so easy to test the liquors.

4. The great quantities of water carry off small pieces of glue stock and gum fat, if catch basins are not provided sufficiently large to allow fat, glue stock, hair and lime to separate from the water: they require frequent cleaning.

It is well known that small quantities of liquid, frequently renewed, and thoroughly drained off each time, effect the most complete and economical washing, and in the shortest time, therefore pits or vats with proper arrange-

ments for stirring, draining, and inspection are in every way preferable. The lime scum from the pits is often used in the manufacture of fertilisers.

To remove the embedded lime, dilute hydrochloric acid (1 or 2 per cent.) is sometimes used, followed by plain water as usual. But in this way fatty acids from the lime soaps are lost, while a careless use of acid allows a great deal of raw gelatine to be dissolved and carried away, especially in horse fleshings.

On the other hand, if not washed properly free from lime, ammonia may be evolved in the boiling. Weak sulphurous acid has been used with advantage.

Hoeveler's glue stock washer (American patent) is designed to remove lime without breaking the material by means of a paddle wheel with spoon-like arms, with a settling tank to gather any particles; the stock can then be dried with the expenditure of very little water for washing.

Washing Salted Stock

must be efficiently performed, as the presence of salt deteriorates the quality and appearance of glue. Salted stock is not used in the manufacture of size. The progress of washing should be observed by testing the liquors at intervals with nitrate of silver in comparison with the water supply; the density of the white precipitate, or cloud, of silver chloride will reveal when the process is finished: this should be done after each portion of fresh water has had time to soak in, say fifteen to thirty minutes after adding. Washing water is frequently warmed to 80° F.: some use the waste water of vacuum pans at 90° to 98° F.

Use of Soda in Glue Making.

When a sheet of gelatine is immersed in dilute soda the solution absorbed by the gelatine contains more soda than

that left behind in the vessel, the amount absorbed being greater with dilute solutions than with strong ones. The same is not the case with common salt. Hence, when treating with soda to remove fat, it must be remembered that the product will retain alkali, which can only be imperfectly removed by washing with water, and may possibly cause injury in the subsequent heating. Soda, therefore, has to be used with caution, and usually only as a supplement to the milder alkali lime.

Fleck, however, considers it better to employ a weak alkaline ley, 2 parts soda and 3 quicklime to 300 to 400 stock.

Milligan, of New Jersey, U.S.A. (English patent, 3393, 1888), washes fresh pieces and fleshings in clean cold water, places them in a basket and plunges into boiling water for less than one minute. This causes the stock to shrink, hardens the tissues and diminishes the weight by over 40 per cent. The stock is now dried in a current of air at 125° to 170° F., then again plunged for ten minutes into a boiling solution of 12 lb. of soda crystals in 100 gallons of soft water to remove fat, washed with hot, then with cold water, and soaked till hard in 1 per cent. alum solution. Finally it is converted into glue in the ordinary way.

Sulphide of Sodium is sometimes used along with lime in the preparation of skins : the stock will usually then show brown, bluish or green stains, due partially to compounds of iron. Treatment with weak acid (hydrochloric of $\frac{1}{2}$ to 1 per cent.) will frequently effect improvement. Careful washing is necessary afterwards, but the sulphur retained in the glue will often occasion trouble.

Glue from Leather Waste.

The fat is eliminated by boiling with soap and soda, and the tannin is extracted by milk of lime or other alkalies.

By continuous washing the alkaline tannate is removed, "the leather becomes hide, and is boiled to glue. The yield of glue from untanned hide being about one-third, that from tanned leather is one-quarter." As the retention of the smallest quantity of tannin prevents the animal tissue from dissolving in water, the operation is rendered quicker and easier by reducing the leather scraps to a coarse pulp in a

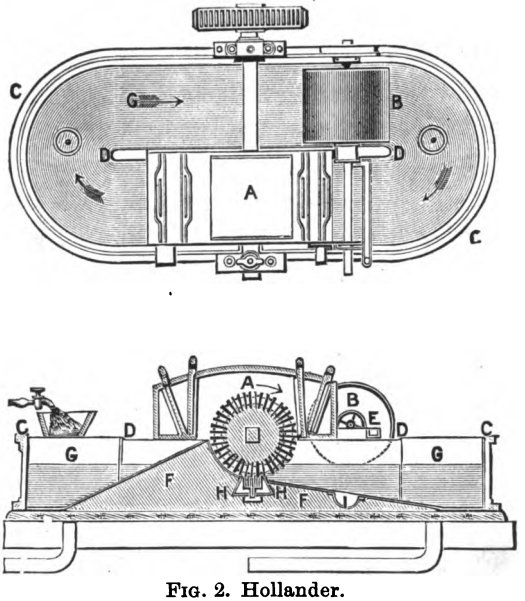

FIG. 2. Hollander.

machine similar to the rag engine (Fig. 2) or "Hollander" used by paper makers, and then heating in a pressure-boiler under a pressure of two atmospheres with 15 per cent. of slaked lime.

Action of Bacteria in Salting and Liming.

The materials for the manufacture of glue—the "glue stock"—are rarely obtained in their fresh state; they have usually been salted, limed, or dried for their preservation. A paper by F. H. Haenlein on "The Action of Salt on the

Putrefying Bacteria of Hides" (Dingler's *Polyt. J.*, cclxxxviii., 214), gives an interesting investigation of the influence of salt (chloride of sodium) both in softening and preventing fouling. Haenlein soaked cleaned pieces of hide in sterile water, and in saturated, 10 per cent. and 2 per cent. solutions of salt, for seven days, in vessels exposed to air. At the end of the time one-tenth cubic centimetre of the solutions was incubated on a gelatine plate. The saturated and 10 per cent. developed only one colony, while the 2 per cent. gave 871, mostly micrococci and non-liquefying: the water alone showed "colonies innumerable, including micrococci, a large number liquefying".

A second series, incubated for eight weeks in closed vessels, gave in the saturated and 10 per cent. solutions no colonies, in the 2 per cent. many colonies but none liquefying, in the water a large number of liquefying bacteria. In the two latter cases the hide was discoloured and soft and the liquid putrescent; in the stronger solutions little visible change had occurred beyond a slight hardening. The alkalinity of the 2 per cent. solution was always stronger than that of the water.

It must be remembered that the salt dissolves a variable quantity of substance which would be available for glue making, therefore reducing the yield from the clippings and waste; also that much washing is required if a concentrated brine has been used, as the presence of an undue amount of salt is very objectionable in glue.

Antiseptics.

Several patents are extant for the prevention of putrefaction during the soaking processes by the addition of preservatives. Only such agents are available as are cheap, on account of the large volume of liquid; they must also not show any tendency to harden the membrane or combine

with it, therefore the selection is limited. Dark-coloured tar products are inadmissible; metallic compounds, such as mercuric chloride, chlorine and hypochlorites are excluded; formaldehyde in weak solution (1 in 10-to 100,000) has been used beneficially. In this small quantity it does not harden the stock, nor affect the subsequent boiling, as it is dissipated by the heat. Boric acid, and its preparations, in spite of their low antiseptic power, have been much in favour. Phenol is hardening, and gives its odour to the glue. The minimum strength required to prevent putrefaction for a reasonable time is :—

Phenol (carbolic acid) . . .	1 in 1000.
Boric acid, about	1 in 200.
Formaldehyde, about . . .	1 in 20,000.

Disinfection of Hides.

In the United States, and some other countries, the departments of agriculture require hides of neat cattle that have not been salted or arsenic-cured, to be disinfected by sulphurous acid, carbolic or corrosive sublimate (mercuric chloride). Under certain circumstances such treatment exercises a very injurious influence on the glue made from trimmings.

Extraction, commonly called "Cooking".

The earliest mode of making glue was to place the stock in a vessel, cover it with water, and place it over a naked fire, but the product was very liable to be dark coloured and of inferior quality through overheating. An improvement was to support the materials on a perforated grid a little distance above the bottom, so as to save them from risk of burning. The water should be gently simmered with agitation. Then the first liquor is run off, fresh water added, and the heating continued. The extraction is repeated until the

solution ceases to gelatinise on cooling. The liquors give glues of different grades, the first being the best.

Fractionated boiling. At first a comparatively small quantity of water is added to the materials, the cover is put on, and the whole boiled about two hours, and the process repeated as described above as long as anything valuable is extracted. The last liquor is kept for use instead of water in a subsequent operation, or is worked up separately. By this method injury by heat is avoided, and the product is better.

High-pressure steam gives a very strong solution in a much shorter time. Its use is more common in England than on the Continent.

Allow to settle warm, a little powdered alum being sometimes added.

Run into wooden moulds, wider at the top than at the bottom. When sufficiently firm, detach from the moulds by a sharp knife, and turn on to a damped table. The block is then cut into cakes of the required size by means of a wire, or by a frame containing a number of such wires fixed parallel at the proper distances apart.

It has been said that it is advantageous to allow the offal to become somewhat decomposed, then disinfect with chlorine or sulphurous acid. We are unable to say whether this is correct.

With reference to the plant employed, four principal systems are in vogue :—

I. *The Open Process.*—Here the heating is carried on exposed to the air in large pans made of cast, or better, of wrought iron (cast-iron pans are cheaper, and rather less subject to corrosion, but are liable to fracture from jars or abrupt changes of temperature). The heat may be applied in five different ways :—

(*a*) *By an Open Fire.*—For the reasons already stated

this method is objectionable, and is now, except on a small scale, almost disused.

(*b*) *In a Water Bath.*—Several large makers treat their materials, with sufficient water to cover them, in large "coppers," made of wrought iron, immersed in an outer vessel containing water, the whole built into a furnace. Every one has observed that in boiling glue in the open air, unless it is continually stirred, a skin forms, and if allowed to pass into the glue would cause those streaks and clouds that are visible in glue cakes that have been improperly made. In this process the skin is dipped out at intervals by large ladles, and is placed finally, with the undissolved

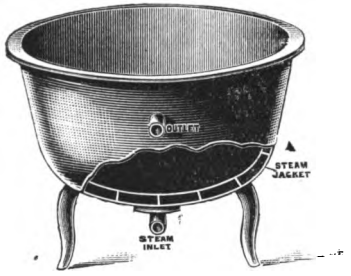

FIG. 3. Jacketed Kettle.

remains of the offal, on a wire strainer, which retains the solids, to be returned afterwards to the copper for a second boil-up with water, and allows the liquid to pass to a clarifying tank.

(*c*) *By a Steam Jacket.*—The pan is made with hollow walls, strengthened by straps and stays, and steam at any desired temperature is passed through. A jacketed cast-iron kettle of this description is shown in the illustration (Fig. 3).

(*d*) *Steam Coils* are used in many processes of manufacture for evaporation and internal heating of a body of liquid. In the glue manufacture they do not seem to have been so successful, on account of (1) the waste of energy by

the friction of the steam in the coil, (2) their cost, (3) leakage of joints.

(*e*) *Forcing Raw Steam into the Liquid.*—The steam must be superheated or condensation will occur in practice. The temperature is apt to be uncertain, and the results unsatisfactory.

Bone glue, made by the open process, is said to be of fair appearance, the first runs being equal to the last runs of hide stock, to be easy to clarify, but to have a very strong animal smell, rendering it unsuitable for certain purposes. It is much better if the stock is previously bleached by sulphur dioxide, which does not injure the oils and fats.

Bertram's Process (English patent, 951, 1892) is distinguished by the low temperature used in extraction. The stock is "cooked" at 160° to 170° F. (71° to 77° C.) in a jacketed kettle or water bath. It makes very good glue, even from sheep stock.

II. *Closed Tanks with Water under* 10 *to* 15 *lb. Pressure.*—Usually two runs are made after the pressure of steam has been reduced, each of two or three hours duration. The liquors are more concentrated, and therefore require less evaporation; the glues, if carefully made, are equal to those of the first process, and do not smell. While open vat cooking produces about 5 to 10 per cent. glue, pressure cooking extracts 10 to 13 per cent. The bone meal yields rather less ammonia (2 to $2\frac{1}{2}$ per cent. as against 3 to 4 by the open method) on account of a certain loss occasioned by the greater heat, but more phosphate (60 to 70 instead of 50 to 60).

III. *French Process.*—The bones without water are heated by steam at 20 lb. in revolving or oscillating tanks. The glue liquor formed by the condensed steam is drawn off constantly as soon as produced. After three or four hours the bones are taken out, crushed, and boiled up further in

open vats. The glue is said to be of best quality, sweet, and equal to any fleshing glue. The bone meal shows 2 to 3 per cent. ammonia, and 50 to 55 per cent phosphate. (See illustration.)

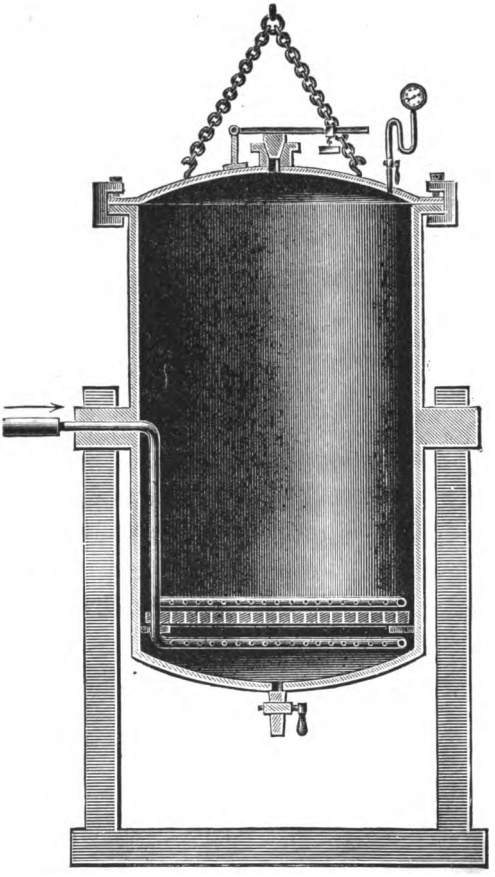

FIG. 4. Boiler for Glue Extraction.

IV. *English Process.*—The bones are included in a steam-tight cylinder and water made to trickle slowly over them whilst steam is admitted from below. So the bones are digested with the minimum of water, and the solution

issues from below in a slightly turbid but nearly colourless state, and only requires clarifying to produce a superior bone gelatine, or at least a high grade of glue. Although somewhat slow, and requiring careful management, this process seems to be one of the best, and can easily be applied to hide scraps or other raw materials. A number of patented apparatus of the kind have a series of perforated alternating shelves or trays.

The following are other processes :—

Huet's Process for Manufacturing Gelatine and Glue.

According to the German patent, 19211, 1881, the refuse used is brought in contact with a solution of aluminium chloride of 2·5° to 5° B. for twenty-four hours, and then kept in heaps till used. On boiling this treated material, all the fat collects on the surface, whereas, in the ordinary treatment of milk of lime, 5 to 7 per cent. of fat is lost.

In the English patents, 5249, 1881, and 134, 1882, the skin of the fatty animal refuse is first broken up, and the crushed material macerated in a tank containing a solution of aluminium chloride of about 10° B. instead of lime. If the refuse contains much fleshy matter, it will require a previous washing, and the chloride bath must be renewed at the end of each operation. After remaining in the liquid for twenty-four hours, the pulp is taken out, drained and submitted to pressure to remove excess of tanning liquid. This treatment secures the crude materials from decomposition on storage. To separate the grease, a small quantity (1 to 2 per cent.) of chopped straw is added to facilitate the flow of the fat, and the materials are then spread upon an inclined hollow plate, heated by steam to a temperature not exceeding 100° C., in a layer 6 to 8 inches thick. They are then submitted to a pressure of 1 cwt. per square yard by another steam-heated hollow plate. Pure fat

escapes first, and then gelatine and water. The residue is placed in a hot press to extract the last remnants of fatty and gelatinous matter, and the resulting cakes may be employed as food for cattle or as manure.

Process for Preparing Glue from "Fish, Whale, and other Sea Animals" (L. A. Groth, London, English patent, 5,786, 1882.)

Soak the fish or parts of the same in warm water, mixed with acetic acid or vinegar, after first freeing the material from all the albumen, salts, and other matters capable of extraction by cold water.

G. W. von Nawrocki, Berlin, patents an apparatus for extracting glue from bones (English patent, 5841, 1884) successively in the same extracting vessel, by (1) a solvent such as benzene for the extraction of all fat, the solvent being recovered by distillation, and used several times; (2) a weak solution of oxalic or hydrochloric acid for a greater or less time, and under more or less pressure according to the age of the bones; (3) hot water for the extraction of the glue. A special feature is a perforated coil or rose in the top of the extractor employed in conjunction with an injector below, the effect of which is to draw off the solvent from below, and flush the bones with it from above. There is also a special method of connecting the extractor with the condenser, the solvent store, and the still in which the solvent is vaporised.

Buttner's apparatus (English patent, 2,615, 1887) is intended for "extracting, washing and condensing glue, oils, and other substances from bones". Three separate modifications for extracting by volatile solvents are described, with special precautions for the complete recovery of the solvent.

Bisulphide of carbon, CS_2, is sometimes used for re-

moving grease, but although a good and cheap solvent, its volatility and inflammability render it dangerous.

When steam direct from the boilers is used for extracting glue, it must be "clean"; that is, free from matters capable of injuring the product, such as sulphuretted hydrogen, ammonia, oils, or empyreumatic substances.

The capacity required in boiling is stated to be "one-tenth more in gallons than the lbs. of stock," *i.e.*, 1 lb. stock to 11 lbs. water. Hot water is run in in the following proportions:—

To 250 lbs. wet stock add 125 gals. water.
To 100 lbs. wet stock add 50 gals. water.
To 100 lbs. dry stock add 90 gals. water.

"Boiled until a sample yields a jelly on removal: about one hour for wet and two hours for dry stock." The level is kept up by adding fresh hot water, well stirring.

F. J. Machalski, Brooklyn, N.Y. (English patent, 5,821, 1894), combines in one apparatus, which is necessarily very complicated, the several operations of extracting fat, boiling out the glue, bleaching, clarifying and evaporation. The raw materials are first subjected in closed receivers to the action of a solvent such as benzene, gasoline, or ether, aided by steam heat, to remove the fat. By an arrangement similar to the well-known Soxhlet apparatus, the solvent is recovered continuously, and the fat run off. Steam is then admitted to the receivers, and in condensing extracts the glue, the solution being forced into pans with steam coils, where it is bleached by sulphurous acid, clarified by alum and soda, and evaporated.

VACUUM PANS AND MULTIPLE EFFECT EVAPORATORS

are much used in America. When, with the object of economy, large quantities of water are used for extraction of the stock, the liquors become so dilute as to require concen-

tration. The boiling point of a liquor is higher than that of water in proportion to the percentage of solid matter, therefore to boil down in the air would much injure the glue both in colour and tenacity. By exhausting the air by fans or pumps, the pressure is so reduced that the boiling point is

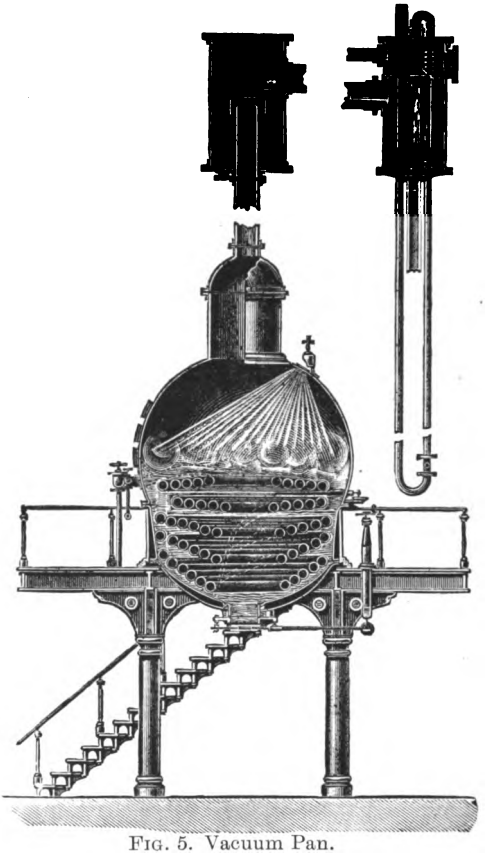

FIG. 5. Vacuum Pan.

greatly lowered, while the evaporation is accelerated. But complaints are made of the great waste owing to spray and froth being carried off in the steam. An American authority states: "We have found in the condenser water of vacuum pans from 0·1 to 0·25 per cent. of dry glue. For each gallon

of liquor evaporated, twenty-five to thirty gallons of condenser water are produced, therefore this means a very large waste of glue."

"Swenson's patent" and the "Yaryan" are much used as multiple evaporators, besides the ordinary vacuum pans such as are employed for sugar boiling.

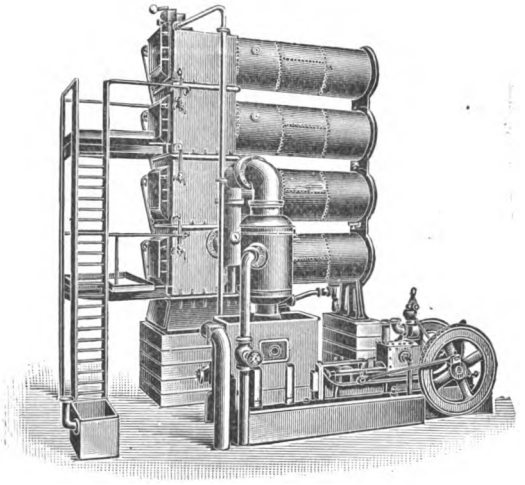

FIG. 6. Yaryan Evaporator.

BONE GLUE: ACID PROCESS.

In the boiling process the gelatine is dissolved out and the earthy phosphates left. In this method, the rationale of which is explained in Chapter I., the mineral matter is removed by acids, and the skeleton of collagen left.

The bones collected from miscellaneous sources and picked are coarsely ground to about three inches in diameter in a bone mill.

The Crosskill Bone Mill (Fig. 7) is intended to be driven by a strap from the fly wheel of the common portable engine now so generally used for agricultural purposes. It consists of a pair of strong rollers made of wrought iron, with

case-hardened cutters, and a revolving or oscillating riddle for separating the ground bones as they fall from the cutters; the whole carried by a substantial cast-iron frame. They will grind from six to sixteen cwt. per hour with a three to eight horse-power engine.

Fig. 8 is a more powerful machine by the same makers (Crosskill): when attached to a ten horse-power steam engine or water wheel it will crush and dress about fifteen to

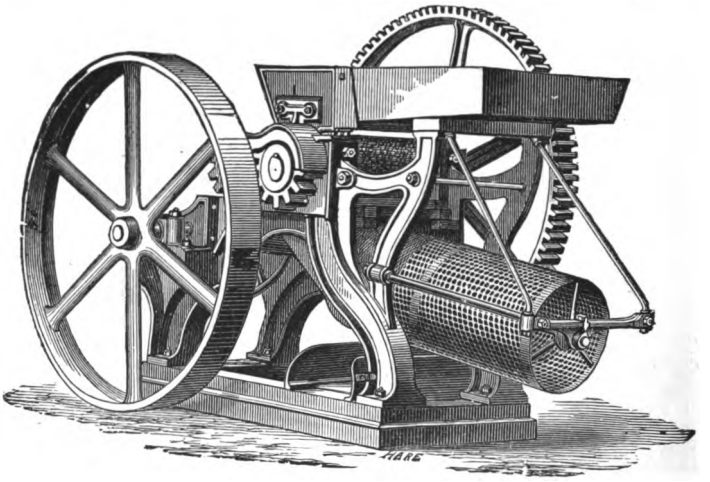

FIG. 7. Crosskill Bone Mill.

twenty tons per day. It has two pairs of rollers with cutters, a revolving riddle for separating into rough, half-inch, and dust, and a friction sheave for preventing accidents to the cutters.

The crushed bones are placed in vats containing cold hydrochloric (or in some cases sulphurous) acid of 7 B. or 1·05 specific gravity (= 10·6 per cent. HCl) for thick bones, or half that strength for thin bones, and digested till they become soft and transparent. Sometimes a renewal of the acid is necessary. The phosphates can be precipitated from the acid solution by ammonia, or the whole evaporated with

charcoal or silica and distilled to make phosphorus. The collagen is well washed with water till all acidity is removed, then placed in a series of closed iron digesters, each about eight or nine feet high, and holding eighteen cwt., where they are treated with steam at two to two and a half atmospheres for three hours, the melted fats and solution of glue

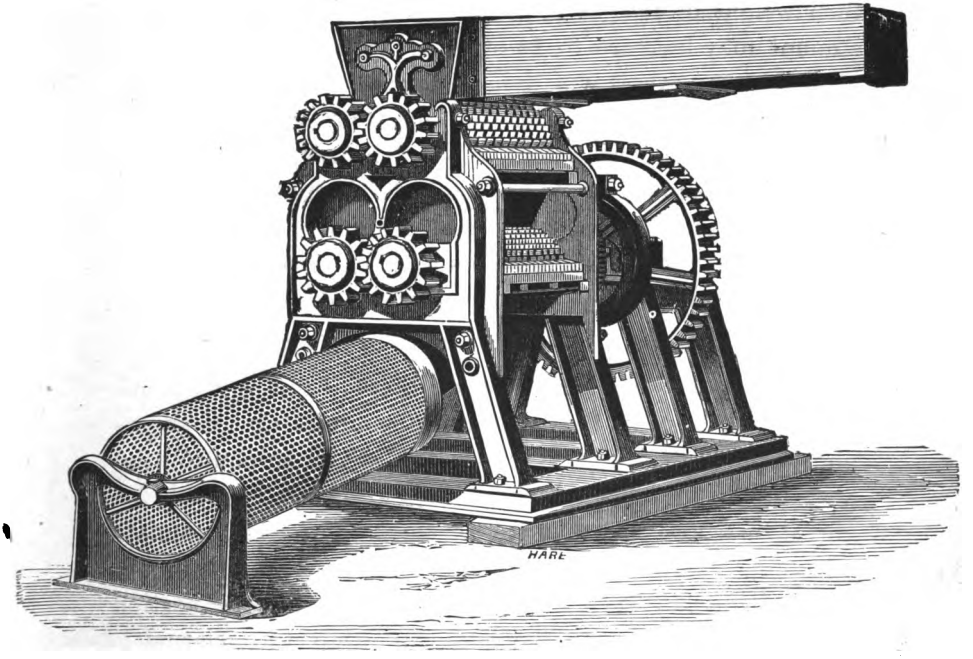

FIG. 8. Crosskill Bone Mill.

being run off gradually into settling tanks, and the rest of the operation conducted as usual.

Davidowsky states that 10 kilos of bones require 40 of acid, that they are covered for eight to fourteen days, then treated with fresh acid.

Sulphurous Acid Process.

The familiar employment of sulphur dioxide in paper making, either as solution or as gas, suggested its use in the manufacture of glue, especially that derived from bones.

When ordinary bones are treated with a current of moist sulphurous acid gas, they absorb from 10 to 12 per cent. of their weight of the gas in the course of twelve hours. The amount may increase to 15 or 20 per cent. on longer treatment, but the excess will then disappear on exposure to air. Messrs. Grillo & Schroeder, of Dusseldorf, who patented this process (English patent, 2175, February, 1894), believe that this is simply due to the calcium phosphate present in the bones, and remark that an absorption of 11 to 12 per cent. on the gross weight amounts to 16 or 17 per cent. of the inorganic constituents, and corresponds to the equation :—

$$Ca_3(PO_4)_2 + SO_2 + H_2O = 2CaHPO_4 + CaSO_3,$$

the sulphurous acid simply acting in the same way as sulphuric acid does in the well-known manufacture of superphosphate, but, being a milder acid than sulphuric, the alteration of the organic constituents which are available for glue stock can be almost entirely avoided. The acid phosphate is soluble in water, therefore the bones after treatment are easily disintegrated by boiling water, when a large portion of the lime remains in the sediment, while the gelatine is dissolved.

The process as commercially conducted is very similar to the well-known "sulphite" method of treating paper pulp, and is carried out in iron cylinders, or better in close wooden vats lined with lead.

The gas is usually generated in an impure form, with a large admixture of air and carbonic acid, by combustion of pyrites and coal, of crude sulphur, or even of only a highly pyritous fuel.

On the other hand, since it is well established that the absorption of a diluted gas is less ready, and is more wasteful than that of a gas in the pure state, the employment of a definite quantity of sulphur dioxide in a concentrated state, either prepared by the regulated burning of sulphur, or the decomposition of sulphuric acid, yields more regular results, and a product of better quality. Liquid sulphur dioxide, which is now obtainable at a moderate price and in quantity, has the advantage that it yields a continuous current of pure gas of any required rapidity by simply opening a valve, and that the exact amount used can be ascertained by taring the containing vessel before and after the operation.

The result of the process is a liquor which has been more or less bleached by the sulphurous acid, and contains a deposit of phosphate and sulphite of lime which require separating. Formerly it was the custom to allow it to deposit and run off the clear liquor, but the adoption of a filter press admits of using less water, and therefore saving the cost of evaporation and the injury to the glue by long heating. While insoluble the lime salts are separated in a concentrated state available for manure. It is necessary, however, for the sulphite, which may amount to 10 or 20 per cent., and is injurious to plants, to be oxidised to sulphate of lime, or gypsum, which is beneficial. The oxidation occurs with fair rapidity when exposed to the air with occasional turning over, but may be facilitated by the action of nitrous fumes or the careful addition of nitric acid, and of lime afterwards for neutralisation, when the "artificial guano" will contain the valuable constituents, phosphate and superphosphate, sulphate and nitrate of lime, and a nitrogenous residue from the gelatine. Another method of dealing with the insoluble residue is to separate by mechanical means any unattacked bone (stated to amount sometimes to 10 per cent. of the original), to return this portion to the cylinders for further sulphiting, then to grind the rest to

powder, and treat it with sulphuric acid as in the manufacture of superphosphate, the evolved SO_2 being used again.

The liquor will be acid, and will require neutralisation with slaked lime. This is better done before the separation of the insoluble matter, as a further precipitate is occasioned. A small amount of calcium sulphite remains in solution in the glue liquor, and is useful by acting as a preservative. Glues for which sulphurous acid has been used, either in the preparation or for bleaching, will reveal themselves chemically by the presence of an unusual quantity of sulphate in the ash.

The necessity for using a fixed quantity of gas is illustrated by the instructions in the above-mentioned patent. It is recommended to use half the number of cylinders or vats for new contact with the current of gas, while the other half, "after an absorption of from 10 to 12 per cent.," are resting to allow of the combination to take place, and are emptied and refilled in turn, the gas being passed in series through the active cylinders. When liquid sulphur dioxide is used, the weight of liquefied gas required will be 1 to 1·2 per cent. of that of the bones, and the vessel must be able to stand a pressure of two to three atmospheres (30 to 40 lb. per sq. in.).

One advantage of the process is that the bones need not be freed from grease beforehand by solvents or otherwise, as the fat easily rises clean from the hot liquor, and can be recovered by skimming or by allowing to cool and solidify, and then removing. The treated bones are extracted three times with successive portions of water aided by steam for two to three hours each, the first and second extractions being usually mixed, the third used to extract fresh bones.

It has been proposed to utilise the crude sulphite cellulose liquors from paper factories in the preparation of glue stock.

For this purpose the liquid contains at first too much lime in the form of calcium bisulphite; this is removed by the addition of more lime in a manner similar to the well-known Clark's method of softening waters, when the calcium hydrate combines with the calcium bisulphite to form neutral calcium sulphite, which is insoluble in water, and can be removed by deposition in vats or by a filter press, the equation being as follows :—

$$CaH_2 (SO_3)_2 + Ca (OH)_2 = CaSO_3 + 2H_2O.$$

The calcium sulphite can then be made to yield sulphur dioxide gas by treatment in closed vessels with sulphuric acid. Or the SO_2 can be liberated from the liquors themselves by the action of sulphuric or hydrochloric acid and steam, but the product is more impure than the first, and very watery. (German patent, 75391, 1893.)

In patent 4356, 1883, several mechanical details of the acid process are described.

Clarifying.

After the extraction, the glue liquor is run into a large shallow vat, in which it is kept warm for a few hours, when the grease rises and is skimmed off, and the flocculent and fibrous impurities settle. The glue liquor can now be drawn off clear, if it has been properly made from sound stock, although the strength is not affected by a slight amount of turbidity. But the liquors from the third extraction are generally very cloudy, and often very dark; they are either at once made into "Russian glue" by incorporating with a white powder, or else must be clarified by subsidence or precipitation. Dilute liquors deposit their sediment more easily than strong ones.

Alum, either alone or followed by a small quantity of milk of lime, has long been used for clarifying. The alkaline sulphate of the alum remains in the glue, which does not

occur if crude sulphate of alumina is used: this salt is cheaper but is often very acid. The whole is heated to drive off the air bubbles, and cause the flocculent precipitate to coagulate: on standing for about four hours the liquid becomes clear. Albumen is sometimes used for the better qualities of glue, and generally for gelatine, but a cheaper substitute is fresh blood, which contains albumen and fibrin. Dry albumen is dissolved in cold water, or white of egg is used direct, if procurable. Before adding either of these substances the liquor is cooled to 54° C. (130° F.), and the clarifier well stirred in; then the temperature is raised to about 93° C. (200° F.) when coagulation occurs, and the precipitate entangles the impurities and falls to the bottom, requiring, however, from twelve to twenty-four hours to clear. It is said that glues clarified with albumen have a characteristic "soapy" smell and show a tendency to foam.

Sulphited glues can be clarified by milk of lime, the calcium sulphite rapidly settling; the liquor must be left slightly acid, or it does not clear.

Cooling.—In some processes the concentrated glue liquor is cooled till set, and the block cut up into sheets by wires fixed in a frame. If the cooling is done slowly the liquefying bacteria will rapidly injure the glue, especially in summer—the most dangerous temperature being about blood heat, or 37° C. (98° F.). Therefore, it is run into metal boxes, made of wood lined with zinc, or better, of stout sheet zinc or heavily galvanised iron. These hold about ½ cwt. each, and are of two shapes: one deep and nearly square, to allow of the settling of liquors containing solid impurities; another long and shallow, for quick cooling of clear liquors. Iron should be kept from contact with the liquor, as it readily rusts, and causes discoloration.

The cooling is effected by a current of cold water, where it is available, but often merely by cold air, aided

by fans or blowers, in a room protected from heat or frost.

On a smaller scale for more expensive goods, the glue liquor is run on to sheets of glass, cooled by water, in layers about ¼ inch thick.

Formerly much of the cooling and drying was done in the open air, with great uncertainty and inconvenience. Large quantities of ice were also used. Several refrigerating machines are now employed, which, by the evaporation of liquefied gases such as ammonia, sulphurous or carbonic acid, reduce a tank of brine to near freezing point. The temperature should not be allowed below 33° or 34° F., as if frozen the jelly is hard and difficult to cut. The brine circulates in iron pipes placed near the ceiling of the room; they must be kept as clear as possible of ice and dirt, and the cooling house should be scrupulously clean and sweet.

Cleansing Vessels, Etc.

A series of two or three vats of hot water being provided, the first one is used for removing the heavier coatings from the small coolers, nettings and ladles, and for dissolving the floor scrapings. When the liquor has become sufficiently strong, it is run into a boiler and used for common glue. The first vat is then filled from the second, which has been used for further washing the utensils. The third vat contains clean water for final cleansing; and may with advantage have an addition of zinc sulphate or carbolic acid as an antiseptic, the water being thrown away when dirty.

Forming and Drying the Sheets.

This part of the process has been considered as requiring the greatest care, and as being the most difficult and

uncertain, whole batches being occasionally spoilt through formerly little-understood causes, most of which, however, have yielded to scientific investigation.

From very early times, the process has been carried out by spreading the concentrated glutinous liquor, at a certain critical point judged by hand tests, as evenly as possible over hempen nets arranged in stages above one another, and dried by a current of warm air. It is clear that the drying of thick sheets in this manner is a slow process, and depends on the hygrometric state of the atmosphere. Souring and mouldiness are liable to appear, and the sheets are often contorted, uneven in thickness, and unequal in quality. In thundery weather it was considered almost impossible to obtain a good product. Glue liquor and jelly absorb ozone with avidity, and are decomposed by it into oxidised products with no gelatinising or adhesive power: this may be the reason why an approaching thunderstorm is reputed to cause great damage in destroying the coagulating powers of the glue soups, or causing the glue to turn on the nets, *i.e.*, to lose its consistency, and become liquid and foul. Crooke's edition of Wagner's *Technology* also speaks of the injurious effect of thunderstorms, without hazarding a reason.

Cotton netting is now common in English factories. But the use of any weak or absorbent material is found to be attended with the following disadvantages:—

1. Being freely handled in the making, it is almost always impregnated with dangerous organisms which penetrate the moist glue cake, and cause moulding or putrefaction. When this occurs, it is attributed usually to a state of the atmosphere, but if the cakes are examined, the alteration will generally be found to originate along the lines made by the netting. The fault could be cured by sterilising the net for an hour at 100° to 120° C. in a hot

oven, but besides the expense, the fibre is thereby weakened. Moreover, the spores of a few bacteria, such as *Bacillus subtilis*, which is widely distributed, and has the power of liquefying gelatine, will bear a heat of 120° C. for over an hour, and still be capable of growing.

2. However smooth the fibre, the glue will stick in places, leaving small remains, which being hygroscopic become "sour," and set up the objectionable bacterial changes in the subsequent batches.

3. Owing to sagging, rotting, souring, or wearing into holes, the life of cotton or hemp netting is so short that the constant renewal is a considerable item. A whole batch is frequently spoilt by the fault of a net. In some works heaps of old netting are found, which become very putrid in the rain and sun, and give rise to mysterious bacterial inroads in the factory. In others they are regularly burnt under the boilers.

4. The considerable overlap or selvedge required for securing the edges of the nets involves a waste of the area, and also some difficulty in refixing.

For these reasons metallic netting has been largely adopted, and zinc is the metal chosen. Ordinary "galvanised" or zinc-coated iron was first used, but it was found that the zinc film rapidly wore away, and the exposed iron rusted and discoloured the sheets. Heaps of rusty galvanised netting accumulated as in the old cotton system, and were even more useless. Many patents were taken out for smooth non-adherent nets punched or cut in diamonds or squares and made of sheet zinc or various alloys, but beyond the expense, they were found to be deficient in strength and liable to corrosion and warping. The best material has proved to be a heavily galvanised iron-wire netting having not less than 15 to 25 per cent. of its weight of zinc. It can be strengthened by longitudinal and transverse wires or ribs.

It must be examined by the microscope to see that it is perfectly free from holes or cracks, and should last at least two years in constant use.

The temperature of drying rooms should not exceed 21° C. (70° F.), or the glue will become fluid again and run through the nets, nor should the air be too dry in the first room or the cakes will become bent or cracked.

In England, and on the Continent, the drying rooms are as a rule simply ventilated lofts, but it is quite possible to provide economically currents of air by fans screened from dust, and cooled in hot weather by the arrangement described in the section on cooling liquors, or warmed slightly in winter. The product is greatly improved, the process quickened, and uncertainty obviated.

In America long drying galleries are constructed, sometimes 250 ft. in length and 6 to 8 ft. square, with travelling platforms on rails carrying the sheets of glue on stout galvanised netting. Wood is found to be a better material for the galleries than stone or brick. The access of dust is a great difficulty.

Continuous Process. It was recognised that thinner sheets could be solidified and dried more rapidly and with greater evenness, and could then be amalgamated in layers if necessary into the thicker slabs which are customary. P. C. Hewitt, of New York, devised in 1894 (English patent, 11,426) a machine for rapidly cooling and forming these compound sheets. (Fig. 9.) The hot glutinous liquid issuing by taps from the boilers is directed on to a species of table formed by six horizontal hollow cylinders, close together and revolving in the same direction, with a current of cold water circulating through them, so that the glue is rapidly cooled and solidified. A very slight film of grease prevents adhesion to the rollers; the sheet at first requires guiding over them, but then passes continuously over an

endless band of wire netting where it is dried by warm air. To make a twofold thickness the band is sloped downwards so as to deposit the sheet on a second sheet, carried on another wire band, and formed in the same way by a run from a lower tap; a steam pipe inserted horizontally between the two sheets just before the junction causes partial melting and therefore adhesion. A number of thicknesses can thus be joined, or a combination made of glues of different qualities.

Another form of Hewitt's machine consists of a horizontal

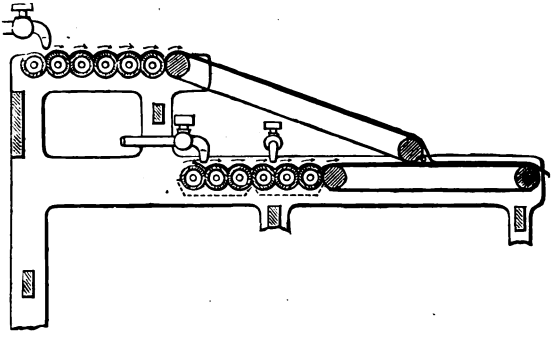

FIG. 9. Hewitt's Machine.

cylinder cooled by water or refrigerated brine, dipping in the glue liquor, and carrying a thin coating of the latter, which rapidly congeals, is detached, cut by knives into the required lengths, and fed on to frames to dry.

Kranseder & Leutsch, of Munich, patented drying trays with longitudinal strips, on which the sheets of glue or gelatine are laid. The trays are made thicker in cross section towards the exit end, so narrowing the spaces and increasing the speed of the air current, thereby causing the evaporation to be uniform.

CRUSHED OR POWDERED GLUES.

In the United States a large proportion of the glue is sent out in the crushed or powdered form, obtained by grinding in special mills. It is easier to use, but is subject to much dirt and adulteration.

Brauer, of Brunswick (English patent, 2400, 1898), prepares a glue in a very porous condition, so that it can be easily powdered, by casting the hot glue from the boilers in small cakes, and then at once exposing to a vacuum; when the glue becomes vesicular, it is allowed to cool and dry.

OTHER PRODUCTS OF THE GLUE MANUFACTURE.

Fat Extraction.—We have described how the fat is removed by boiling, steaming, draining, pressure, or solvents, and also many patents for the purpose. While it is necessary for some applications that the glue should be entirely free from grease, the density of bones and their gelatinous basis render complete removal very difficult. Boiling with water and skimming give very imperfect results, as much of the fat remains emulsified. Extraction of the original bones in the ordinary manner with benzene, bisulphide of carbon, ether, or light petroleum is equally incomplete. In Seltsam's process the solvent is boiled with the bones (previously coarsely crushed and the dust sifted out) in a strong closed vessel, so as to obtain a higher temperature, greater penetration, and avoidance of loss. The vapour ascending condenses in the pores, extracts the fat, and collects under the grid at the bottom as a layer of solution which is subsequently distilled.

Leuner's apparatus works on the Soxhlet principle, without pressure (Fig. 10), using solvent and steam simultaneously. The crushed bones are placed in J above the perforated false bottom, M. C is a steam pipe, by means of

which the bones are steamed as a preliminary, the surplus steam escaping through the exit pipe, Q. After steaming, water and benzene are run in from the reservoir, L, into the space under the false bottom, and heated up by the steam coil, O. The evolved vapours are condensed in the worm, A, and at first run back over the bones through the cock, F, the vapour passing upwards to the worm through D, and the condensed liquid being divided into separate streams by the

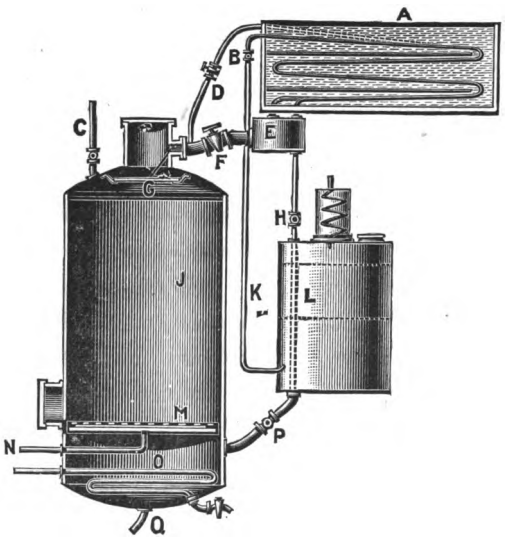

FIG. 10. Leuner's Apparatus.

spreading plate, G. After some time the cock, H, is opened, so that the condensed liquid runs into the reservoir, L, instead of flowing back into J. When all the solvent has been volatilised nothing but water condenses in the worm, which is known by means of a sampling cock attached to J; the draw-off cock, Q, is then opened, and the watery gelatine solution and oily matter run off into a suitable separating receptacle; J is then discharged through a manhole and refilled, and the whole operation repeated.

Bone fat, or bone grease, differs much in character according to the preparation. From fresh clean materials, as obtained in the manufacture of gelatine, it is white or yellowish, soft, and has little odour or taste. Its melting point is given by Schaedler as low as 21·2° C., so that it is liquid in summer, hence it is often called "bone oil," a term also applied to the product of destructive distillation (see below). Lewkowitsch describes it as "not readily turning rancid, for that reason a valuable lubricant". But it is chiefly used for mixing with neat's foot and other oils.

Most of the crude bone grease of commerce is, however, dark coloured, unpleasant in odour, of much higher melting point (bone grease 44°, tallow 46° to 50° C.), and contains free fatty acids. It is used for coarse lubricants, or bleached for candle making. It generally retains phosphate of lime and other calcium salts, which must be extracted before it can be used for soap making. It is therefore placed in a lead-lined tank with a sufficient quantity of dilute sulphuric or hydrochloric acid, and steam blown through to agitate it thoroughly. Sulphuric acid is cheaper and acts less on the lead, but forms an insoluble deposit of sulphate of lime.

The residue, after extraction of glue and fat, still contains about 5 per cent. of organic matter. It is treated with sulphuric acid for the manufacture of superphosphate or used directly in compounding artificial manures.

Spoilt bones and waste unfitted for glue are submitted to destructive distillation in iron retorts, yielding (1) inflammable gases, (2) bone—or Dippel's—oil, a dark-brown fetid mixture of ammonium salts and a number of organic compounds, including phenol, aniline and pyridines (on redistillation a tarry mass is left which is employed in making Brunswick black), (3) a final residue of animal charcoal.

CHAPTER III.

USES OF GLUE.

In this connection the qualities most in demand are:—

1. First and foremost *tenacity*, or the power of resisting rupture. This is ascertained by the methods given in the section on Testing, Chapter V.

2. *Elasticity*, or absence of brittleness, and power of yielding or stretching slightly without fracture. A glue which is too hard, or made with too little water, may resist an enormous strain if applied steadily, and yet will break with a lower force coming with a sudden jerk. A sample that is somewhat elastic is preferable in all cases except where very hard wood is used with the view of great rigidity: even in this case the end is better attained by clamping or by a dovetail joint. In applying the weight in the testing machine, it will be noticed by the movement of the lever that an elastic glue gives way slowly before it breaks, whereas a harder and more brittle one resists up to the point of sudden fracture. Therefore, a good idea may be formed in this way of the elasticity. A more exact determination may be made by the apparatus used for testing this quality in iron and steel bars, but the operation is rarely required.

The strength of glue, if well used, is generally greater than the wood which it unites, so that the fracture takes place through the wood and not through the glue joint.

3. *Covering Power.*—This is a very important matter, as it controls the economy in use. It is ascertained by considering three factors: the water-absorption, the tenacity of the jelly, and the viscosity of a solution of known strength. The verdict of these numbers is usually in the same direction; in the few cases, where they differ widely in their indications, it may be suspected either that the testing has been at fault, or that, as has often been found, the glue has possessed some peculiarity which in practical use has made it of less value. At any rate, if the three factors are ascertained, a sure judgment can be formed of the value. It would be well if buyers were to inquire for, and make themselves acquainted with the meaning of, these constants, and be able, as far as possible, to verify them in the workshops, instead of trusting to trade descriptions, or to prices, which, as we have explained elsewhere, are often artificial.

4. *Keeping Qualities.*—Although this is here less indispensable than in some other uses of glue, considering that the right quantities are better made up when wanted, it is inconvenient when a made glue that has to be kept turns sour or mouldy directly, or the same thing happens to joints in damp weather. Some liquefying bacteria, or their spores, such as *Bacillus subtilis*, are not easily destroyed by heat, and, if present in the interior, are quite capable of rotting a recent joint away: when it is dry, and properly set, they can hardly enter from the outside.

Colour, except for fine cabinet and inlaid work, is of less importance. Dark glues are generally preferred by carpenters, as stronger in proportion to price. A lighter article has either been made of selected material, therefore it is expensive, or it has been bleached, and has probably been reduced in strength.

The ordinary glue pot is sufficiently familiar. It is practically a water bath, consisting of an outer iron vessel of

water, into which fits the inner receptacle for the glue. The adoption of this, the earliest form of water bath, and still the only one universally known, is due to the knowledge that glue must not be heated over an open fire, or it would burn, and that undue heating damaged its setting and adhesive properties. For the latter reason there is doubtful utility in the practice sometimes recommended of adding salt or chloride of calcium to the water to raise its boiling point, under the plea that the glue must be used hot. I have found that a temperature of 70° or 80° C. (156° to 178° F.), which is easily attained by a bath of water alone, is the least injurious to the chemical and physical properties of the glue, while it is hot enough for any work when quickly done. The habit of "boiling well" and of using "blazing hot" has led to much bad and brittle work. The salt or chloride of calcium mentioned above rapidly corrode the iron. Even water must not be left standing in the outer vessel, and if the use be intermittent the inner receptacle should be boiled out in a saucepan, and the whole cleaned and dried for the reception of new glue in the quantity required, and that only.

The best method of preparing glue for use, where there is time, is to first break it with a hammer, then to beat it in a large iron mortar, covered with a cloth or a piece of cardboard with a hole in the centre for the pestle, until the largest pieces are about the size of peas. Any trouble spent at this stage will save time in the next. Cover it with five to ten times its weight of cold water, according to the consistency required, and let it stand, covered from dust, in a cool place for some hours, or even overnight. By this treatment, if it is good glue, it will become soft and much swollen, with clear water above: if liquefied, with water foul and turbid, it is bad and should be rejected (Chapter V.). The water being poured off, any hard lumps are picked out and soaked in water a

little longer. The soft mass is transferred to the glue pot and melted without adding more water. It is usually kept near the boil for about fifteen minutes before using. Any remainder becomes on cooling a very stiff jelly, which can be *just* warmed up two or three times without injury. A wire across the inner vessel enables the brush to be cleared. It is better, wherever possible, to heat the wood, short of warping, than to overheat the glue. The layer should

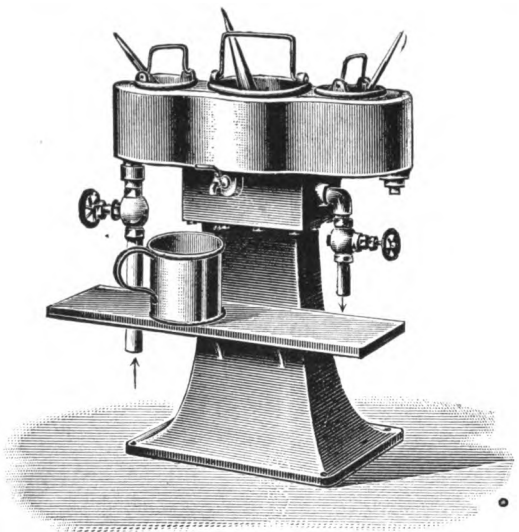

FIG. 11. Glue Oven,

be spread steadily and evenly, seeing that there are no air bubbles: the pieces of wood are then pressed together, and, if possible, tied or clamped. The excess of glue may be carefully scraped or sponged off, but except in corners it is better left on till cold, as it makes a firmer and more air-tight joint, and enables one to judge when the glue is sufficiently set, which takes one to three days, according to the season. Within limits, the closer the wood surfaces are brought in contact the more permanent the adhesion. The matter must

of course be learnt by practice; we merely wish to indicate the principles. The adhesion to resinous woods, as yellow pine, is promoted by first chalking the joints.

Where large quantities of glue are required, the outer jacket is heated by steam. "Richard's Steam Glue Oven" is an apparatus in use in many workshops, and is represented in the figure.

In No. 1 size the central pot, used for melting, holds 1 gallon, the end ones $\frac{1}{3}$ gallon each. In No. 2 size the pots are all 2 gallons. The floor space occupied is, in No. 1, 3 × 2 ft.; in No. 2, 3 × 3 ft.

Copper glue pots are quicker in heating, but are liable to turn green and be corroded by the slightest acid in the glue. Well tinned iron is preferred in most workshops. China is slower in heating but is cleaner; sometimes, however, when left to cool, the contraction of the glue will actually chip away portions of the material.

Veneering.

The foundation wood is smoothed, then finely and regularly roughened by a toothing plane or machine, or even a file or rasp for small work. Size (1 part good Scotch glue with 50 of water) is applied hot, and any defects made good by stopping with a thin paste of fine plaster of Paris and hot glue. When dry, the surface is again levelled. The glue is then spread on the foundation wood quickly, but with great care as to evenness. For large work revolving brushes are used. At this point the fault of frothing, or "foaming," which attends some otherwise good glues (Chapter V.) becomes prominent; it almost certainly depends on the presence of viscous bodies such as mucin or the slimy substances into which glue is converted by long heating, as described in the first chapter (p. 9). It would be interesting to examine whether samples which show a divergence

between the indications of the shot (jelly) test, the absorption of water, and the viscosity, show also a difference in the tendency to froth.

The fault of foaming has occasioned considerable trouble, and at once condemns a glue for certain purposes, whatever grade be claimed for it, and quite independently of its cost. In America, where application of glue by machinery on the large scale is commonly practised, it is said that "while a large number of glues made in the States have this drawback, none of those coming from Europe are free from it".

The causes assigned in the trade are :—

1. Prolonged cooking.

2. The presence of hydrate of lime through careless or insufficient washing after liming.

3. Use of acids in cooking, bleaching or clarifying.

4. Zinc salts, or even zinc white as used for "coloured glues" (p. 20).

Before the glue chills the veneer is laid on and caused to adhere either in the *dry way*, by pressing with a heated piece of wood called a "caul" cut to the shape of the surface, or in the *wet way*, by damping with hot water while the glue is still liquid, and tapping and rubbing with a kind of mallet called a "veneering hammer," and with hot irons, till the excess of glue is squeezed out at the edges. The work is now weighted till dry, again sized, smoothed and polished.

Paper Making, etc.

To make the surface less porous, paper is either "engine" or "tub" sized. The former is effected with a resin soap, the latter by passing the sheets through a warm solution of gelatine or of light-coloured glue, which must not be acid, and should be nearly free from smell. Paper makers are said to have a strong preference for German Cologne glue and its imitations.

Animal Size for Paper Making

must be drawn off with the least possible amount of heat. According to Clapperton, when three or four extractions are made it is a good plan to run off the first from one pan at the same time as the last from another, so that by mixing the two the strength may be kept uniform.

Soap and alum are also added, the former to improve the finish and feel of the paper, the latter to make the size keep better as well as to make it penetrate more easily, besides giving more solidity and hardness. It has, however, an action on certain colours.

Paper has frequently an unpleasant odour derived from the size, which, even when made from the best grades of hides, is not entirely free from smell, but when low grades are used, mixed perhaps with cheap glues, the odour is often offensive.

Prepared Casein is also largely used for sizing. A company is being formed in America for manufacturing it on a larger scale than hitherto for this and other purposes.

For wall papers the glue need not be of high grade, but should be of good colour, and especially free from grease (see (Chapter V., Grease Test). Paper-box makers require a low grade glue, of fair colour, drying slowly—because of warping —and free from strong odour.

Straw hat makers usually employ the best grade of hide glue, of light colour and inodorous: it must not be affected by oxalic acid, so that lime must be almost absent.

Bookbinding.

For the better classes of work the glue should be naturally pale and strong and without marked odour. Some inferior glues which have been chemically bleached turn almost black

in the pot, owing to the bleaching agent not having been properly removed or neutralised. They are generally classed as "French," although this may be considered as a trade name rather than as referring to the country of origin. Besides the water and other tests (see Chapter V.) the use of litmus paper should never be neglected. Any glue which, after being soaked in distilled water, sensibly reddens blue litmus, is unfit for better work, as it will injure many delicate colours. It has been proposed to use chondrin glue, as chondrin, not being precipitated by corrosive sublimate (mercuric chloride), one per 1,000 of this antiseptic can be incorporated with the glue, to keep away the parasites which cause so much damage; volatile compounds, like camphor and essential oils, may also be added, but the odour is open to objection. Mercuric chloride is one of the most powerful of disinfectants; it is inodorous, but is very poisonous, and is apt to cause discoloration, either by reduction, by the action of sulphuretted hydrogen from the air or gas, or by acting on sensitive pigments. It precipitates ordinary glue, therefore, cannot be used with it.

It is recommended that, in preparing glue, a few cakes should be broken in pieces and placed in water for twelve hours, then boiled and turned out into a pan to get cold; when cold pieces may be cut out, and placed in the glue pot as wanted. It should be kept protected from flies and dust. Glue should always be used as hot as possible, but not kept hot longer than is necessary, as it loses strength in the way we have described (Chapter I.).

Zaensdorf (*Art of Bookbinding*, p. 93) recommends that while "paste should always be used for Morocco, calf, Russia and vellum, all leather with an artificial grain should be glued; the turning-in may be with paste. The glue gives more body to the leather, and thus preserves the grain." The old binders of white vellum books gave the boards a thin and even coat

of glue, which was allowed to dry before putting on the covering. *Roan* should be covered with glue, and turned in with paste. *Cloth* is covered by gluing all over and turning in at once: gluing one cover at a time, and finishing the cover of each book before touching the next. *Velvet* should be covered with very clean glue not too thick, first gluing the back, and letting that set before the sides are put down. The sides should next be glued, then the velvet laid down and turned in with glue. Any finger marks may be raised by holding the book over steam, and carefully using a soft brush. *Silk* and *satin* are first lined with thin paper cut to size, and fastened with thin clean glue. When dry, the book is covered in the same way as with velvet.

The same authority warns us that *calf* is liable to be stained black by glue unless certain precautions are taken which are described (p. 88): all glue must be removed from the back and sides before covering with calf. Morocco may have the back glued, as it will not show through, and will facilitate the adhesion of the leather.

In fastening together the sections of a book at the back, a commoner grade of glue is often used: it is to be applied with a brush, and not as in some shops with a handful of shavings, which is a very clumsy and wasteful practice. In Germany the glue is rubbed in with a special hammer, and the surplus taken off with a brush. The drying should be effected spontaneously in a press in a dry room free from dust, and never by artificial heat.

Size for finishing and gilding was formerly made from vellum scraps, but can now be bought ready for use, or made from a thin solution of a pale glue. If too strong, it will make the work brittle: some papers require a stronger size than others. The following receipts for bookbinders' size are given:—

No. 1. Water, 1 quart; powdered alum, ½ oz.; Russian

isinglass, 1 oz.; curd soap, 20 grains. Simmer one hour, strain through linen or a fine sieve, and use while warm.

No. 2. Water, 1 gallon; best glue, ½ lb.; alum, 2 oz. Prepare and use as above.

No. 3. Water, 1 quart; isinglass, 2½ oz.; alum, 120 grains.

Compositions for Printing Rollers

all contain gelatine or glue. The following receipts are used:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Glue . . .	8	10	4	2	32	2	1	3
Treacle . . .	12	...	8	1	12	6	2	8
Paris white . .	1	...	...	...	...	...	...	1
Sugar . . .	...	10	...	...	...	...	...	...
Glycerin . .	...	12	...	...	56	...	...	...
Isinglass . .	...	1½ oz.	...	...	...	...	...	...
India-rubber in naphtha . .	...	...	...	...	10	...	...	...

A patent roller composition is thus made: 32 lbs. of gelatine and 4 lbs. glue are softened in cold water and melted in a glue boiler. To this is added 4 lbs. glucose, 72 lbs. glycerine and 1 oz. methylated spirit. The whole is then digested for four to six hours and cast into rollers. This composition is claimed to be unaffected by temperature, to retain its elasticity and not to shrink.

In practice, it is found that all these compositions from the cleansing and remelting become gradually sticky and useless.

To partially overcome this difficulty, formaldehyde is added to the roller composition, which renders the gelatine insoluble in water, and so prolongs the life of the roller.

Very similar compositions are used for the beds of hectographs. Chrome glue will be spoken of under Gelatine in Chapter IV.

Glue in the Match Manufacture.

A very large quantity of glue is used for this purpose, especially in England, where it is about the only binding material employed. Very much depends on the quality of the glue and its drying properties; even the colour is important as affecting the bright appearance of the article. The "dipping composition" for matches containing vitreous or ordinary phosphorus is a bath of glue of 25 to 50 per cent. strength to which the requisite amount of an oxidising agent, like potassium nitrate or chlorate has been added, kept at a temperature of 38° C. The phosphorus is cautiously put in; it melts, and is stirred to an emulsion, when the sand, glass, or other friction agents are incorporated. The object of the glue is to protect from oxidation, without diminishing the sensitiveness. Match factories in the United States are said to prefer "Irish glues" as they "mix easily with the phosphorus, and stick well to the wood".

Glue is also used as the binding material in the heads and rubbers of safety matches.

Sand, glass, and emery papers and cloths are made by coating the surface with a thin uniform layer of strong glue, and sifting the powder evenly over. Very common or over-boiled glues have a sale for fastening the bristles of cheap brushes for toys and for sticky fly-papers.

Glue and Gelatine in Substitutes for Other Materials.

By appropriate means and mixtures, glue can be rendered insoluble and either soft, pliable, and elastic, or so hard as to be capable of being worked with a lathe and polished. It is not surprising, therefore, that glue and gelatine have been made the basis of a multitude of inventions for imitating

leather, caoutchouc, woods, or even stone, to be moulded, stamped, or carved, for objects of art or even of utility. Cheapness and facility of working are the main conditions, since none of these preparations can be equal in durability or strength to the natural products, while many of their physical properties are essentially different.

Ive's patent, No. 28,817, 1898, mixes gelatine, glycerine, potassium bichromate (to cause insolubility) and ground cork, and moulds by heating to the required shape. "Elastic, tough and insoluble."

The sulphonic acids obtained by the action of fuming sulphuric acid on petroleum, mineral wax, or rosin oil have the property of precipitating glue or gelatine from slightly acid solutions, forming an elastic caoutchouc-like mass, capable of being rolled or drawn into threads. (English patent, 19,502, 1890.)

The addition of ichthyol oil, obtained by the distillation of bituminous shales containing fossil fish-remains, to a mixture of gelatine and glycerine is said to give a compound "closely resembling rubber, and even more elastic". (English patent, 7,745, 1898.)

Leather and Art Work.

Leather waste and cuttings accumulate in great quantities. They can be utilised in several ways.

(1) Freed with some difficulty from tannin, etc., they are converted into glue as seen in Chapter II.

(2) Taking a considerable time in rotting, they furnish a slow, very lasting manure, but not free from danger, owing to the chemicals sometimes present.

(3) For making cyanides.

(4) For consolidating artificially.

Rapeaud (English patent, 8,221, 1888) ground them to a fibrous paste in the following proportions:—

Leather refuse, 78 to 90; gelatine, 4 to 8; tallow, 1 to 2; glycerine, 5 to 12; forming into plates which were dried and calendered.

Boult (English patent, 15,404, 1897) grinds leather paste and glue with hemp, flax or jute to give a fibrous structure.

Other patents for artificial leather are: Thiele and Stocker (English patent, 8,960, 1895).

An emulsion of 5 parts of bone glue in hot linseed oil or glycerin and paraffin is well mixed by agitating in a closed vessel with a solution consisting of 5 parts of caoutchouc and 10 parts of resin dissolved in 100 parts of carbon bisulphide and a little spirit. This mixture is then worked up in a rag engine with 50 parts of finely divided cotton or wool fibre, and 50 parts of ground ivory, cocoa or para nuts, previously boiled in glue solution and dried. Five parts of carbonate of lime, and, if required, colouring matter are added to the mass in the rag engine, and it is then air-dried for some hours, and rolled to the necessary thickness. The product is then treated with a mixture of concentrated nitric and sulphuric acids, washed, dried, and again passed between rollers heated to 50° C.

Schmiedel, Austria (English patent, 8,847, 1895).

For bookbinding, or other fancy work, cotton or linen fibre is glued on to stout paper, calendered and lacquered, coloured or embossed.

Billing and Latelle (English patent, 22,965, 1896).

Cotton wool or other fibrous material is treated with a mixture of gelatin and methylated spirits or naphtha, and rendered pliable by the addition of treacle or glycerin, and after being dried it is subjected to a bath of formalin, alum, or tannin to harden the gelatin. It is then washed, dried and embossed, etc., in the usual manner.

Conn, Mudon and Hall (English patent, 30,357, 1897).

Gelatine mixed with enamel pulp, glycerine, spirit, shellac,

formalin and colouring matter. Prepared in thin sheets and backed with some fabric.

Moerch, Denmark (English patent, 4,235, 1899).

Vegetable fibres and wool, saturated with a compound of linseed oil, resin, turpentine, glue, casein and wax, with a small quantity of borax and bichromate of potash, soaked in acetate of alumina, dried and pressed between heated rollers: the product is said to closely resemble sole leather and to be worked like it.

CHAPTER IV.

GELATINE.

THE chemical reactions of gelatin may be here noticed; most of them also apply to glue solutions, and some have been already given in Chapter I.

In warm solutions, or in those sufficiently weak to be not gelatinous, acids, alkalies,[1] and most mineral salts (such as those of Al, Fe, Cu, and Pb) occasion no precipitate. Chondrin gives precipitates with most of these.

Phosphomolybdic or phosphotungstic acids cause voluminous precipitates, the complete separation requiring twelve to twenty-four hours: the nitrogen can be determined in the precipitate, but includes other substances besides gelatine.

If the solution be evaporated to near dryness, and then treated with a saturated solution of ammonium, magnesium or zinc sulphate, the gelatine is thrown down in stringy masses, along with the albumose, but not the peptones: the latter are almost absent in good gelatine; this process is therefore valuable quantitatively.

On adding a saturated aqueous solution of picric acid, a precipitate is produced which dissolves on shaking, but is rendered permanent by further addition of the reagent. On heating, the precipitate dissolves, reappearing as the solution cools; on shaking, a yellow sticky mass is formed,

[1] Bone glues may give a turbidity with alkalies, owing to phosphate of lime.

leaving the liquid nearly clear. (Nearly all proteids, except mucin, give at once a permanent precipitate.) This behaviour is peculiar, and may be occasionally useful for the recognition of gelatin (Allen and Tankard).

Platinic chloride, mercuric chloride in excess, and basic lead acetate, throw down gelatine more or less completely.. Acetic acid and potassium ferro-cyanide give no reaction.

Copper sulphate and soda give a violet-blue colour, the so-called *biuret reaction.*

An acid solution of chromic acid is said to precipitate gelatin, but not peptones.

Chlorine water in excess produces a turbidity with very small quantities of gelatine. If a current of chlorine be passed, *in excess*, through a solution containing not more than 0·2 to 0·5 per cent. of gelatin, a very insoluble flocculent precipitate is formed, which, after filtration and washing, may be dried *in vacuo* and weighed ; or the nitrogen may be determined in the washed compound without drying. This process throws down all albuminoids, but not bases such as creatine. The weight of the chlorine precipitate, multiplied by 0·74, gives the amount of dry and ash-free gelatin in the solution. If the nitrogen be determined, multiplying by 5·5 will give the weight of gelatin present. For further details see a paper by S. Rideal and C. G. Stewart in the *Analyst* for September, 1897, also on the use of *bromine* for the same purpose, by Allen and Searle, in the October number.

By artificial digestion, or the action of acids or of bacteria, gelatin passes into *gelatoses*, similar to the albumoses from albumin, and *gelatones*, or gelatine-peptones. The latter do not form a jelly. For Klug's investigation of these substances see *Centr. Physiol.*, iv., 189 ; *Chem. Soc. Abstracts*, Feb., 1891, p. 232. He obtained in addition 5·7

per cent. of an insoluble residue, *apoglutin*, and gives the elementary composition of the three bodies as:—

	C.	H.	N.	O and S.	Ash.
Glue . .	42·75	7·00	15·61	34·64	0·88
Apoglutin .	48·39	7·50	14·02	30·09	5·22
Glutose (gelatose)	40·06	7·02	15·86	37·06	2·14

Physical Properties of Gelatin Solutions (Bayley, *Brit. J. Phot.*, xlv., 764).

Bayley finds that the setting point of a solution of gelatin is about 8° C. lower than its melting point; and the rise in melting and setting points according to the percentage of gelatin is more marked in dilute than strong solutions. It is well known that by prolonged heating above its melting point of a gelatin solution its setting power is gradually diminished until it remains liquid at ordinary temperatures, but the melting point of good gelatin is at first slightly raised by boiling. Bayley states that the time of boiling may be approximately estimated by the change of colour. About 150 cc. of formalin per litre prevents the remelting of a 5 per cent. solution of gelatin. The addition of alums considerably lowers the melting point of a solution of gelatin.

Preparation of Liquid Gelatin (Mills' patent, 8,847, 1895).

Gelatin is permanently liquefied by digesting at 100° C. with five times its weight of water, and one-twentieth of its weight of slaked lime for two hours. Other fixed alkali may be used instead of lime, and the proportion is varied according to the quality of the gelatin.

In this patent, use is made of liquefying bacteria, such as *B. liquefaciens* for permanently liquefying the gelatin. A 10 per cent. solution of gelatin, containing a small quantity of meat extract, and a trace of carbonate of soda to hasten the growth, is inoculated with the liquefying organism and incubated at about 25° C. for a few days.

The products from either process are claimed to be of

value as " gums, thickeners, detergents, emulsifiers, and media for photo-lithographic and other photographic purposes ".

Gelatine in Photography.

In gelatine for photographic purposes, purity, neutrality, absence of colour, and indifference to the silver and other salts used, are the chief requirements. The presence of chondrin, according to Colonel Abney, is very objectionable: the chrome-alum test for this impurity is given under Chondrin in Chapter I. M. L. Soret (*Archives des Sciences Phys. et Nat.*, x., 139; *Comptes Rendus*, xcvii., 642) and W. N. Hartley (*Chem. Soc. Trans.*, 1887, 58) have investigated the optical properties, particularly the transparency to actinic rays in and beyond the violet region, which is of very great importance. The latter observer states that " the examination of specimens of gelatine shows that the difficulty of obtaining photographic plates sensitive to the most refrangible rays lies entirely with the character of the gelatine. Ordinarily the spectrum extends to wave-length about 2,146 Cd. Some plates prepared many years ago by Wratten & Wainwright, called ordinary dry plates, were used for photographing a series of metallic spectra which extend to wave-length 2,024 Zr, and there was little doubt that they were capable of receiving impressions of lines still more refrangible. Since then plates of every kind by every maker have been tried, but most of them transmit nothing beyond 2,146 Cd. A sample from Mawson & Swan was recently found to photograph as far as 2,024, but half a dozen other batches from the same makers were deficient in this respect, although supposed to be of exactly the same character. As the plates were prepared in precisely the same way there can be no doubt that the difference was in the gelatine, which must have contained some very slight trace of impurity which could not otherwise be detected." The method of

experimenting adopted was to allow the liquid to dry on plates of quartz (which are almost completely diactinic, or permeable to the rays), and then to photograph the spectrum transmitted by the films. Hartley also examined :—

" (1) A yellow specimen sold for photographic purposes, said to be of Nelson's manufacture, but without any distinctive label. A solution, containing 5 per cent. of the solid and 1 millimetre in thickness, was allowed to dry on a quartz plate. It transmitted a continuous spectrum to wave-length 2,265, but beyond 2,313 the rays were weak.

" (2) A very fine colourless sample made in sheets, which in the original form transmitted all rays to 2,265." Dried as above on quartz, it transmitted all rays to 2,265 in full intensity. He finds that gelatine differs from albumin, casein, and serin ; while the former is highly diactinic, and shows no absorption bands, the latter give absorption bands as follows : white of egg, 2,880 to 2,650 ; pure albumin, casein and serin, 2,948 to 2,572.

Gelatine plates in photography were first used by W. H. Harrison in 1868, while experimenting on the lines of Sayer and Bolton, using gelatine instead of collodion, but with only limited success. Dr. Maddox, and afterwards Dr. Burgess, made and sold a gelatine emulsion which was the first practical formula used.

In 1878 Kennett found that by keeping the emulsion before coating the plates at 90° F. for some days, the speed was so increased as to admit of instantaneous exposures; subsequently the process was shortened by boiling the emulsion with part of the gelatine and adding the remainder. Monkhoven, in 1879, found that ammonia also increased the speed of the emulsion.

The incorporation of small quantities of certain dyes, such as eosin and some oranges and yellows with the gelatine film, affects the sensitiveness of included silver salts

to different rays of the spectrum. This is called "ortho- or isochromatic" printing.

In English patent 11,821, 1895, a layer of resin is applied to assist the stripping of the gelatine coatings from paper supports in the manufacture of photographic films.

Effects of Lead Nitrate and Ammonium Sulphocyanide.

A solution of lead nitrate at the ordinary temperature dissolves gelatine; a concentrated solution at 25° C. dissolves 24 per cent.

In ammonium sulphocyanide it is still more soluble; 5 grammes of the salt in 10 cc. of water will dissolve 5 grammes of gelatine; 100 cc. of water with 1 gramme ammonium sulphocyanide at 23° C. dissolves 2½ grammes of gelatine.

This salt, therefore, which is much used in fixing baths for gelatine plates should not be made up too strong.

Silver bromide is appreciably soluble in gelatine solution, giving an opalescent liquid, reddish by transmitted light, and forming on glass an almost perfectly transparent layer.

Size

includes such inferior gelatines as are used, not for adhesiveness but for "body," in filling porous surfaces such as wood or plaster, stiffening and weighting textile fabrics in paper manufacture, and as a foundation for oil paints or varnishes. The name applies to the kind that is sent out as a jelly, or *tub size*, and to that sold in dry cakes, which are usually thinner and less coloured than those of glue. Even the best sheet gelatine is used for some fine purposes. Many sizes contain much chondrin, which for this purpose is not considered to be disadvantageous.

An outline of a simple process used in an English factory devoted to making tub size may be interesting.

The material is obtained from the tan-yard ready limed and freed from hair, and consists mainly of "faces" of

bullocks or cows (the noses being cut off as food for dogs). It is soaked again in weak lime water and re-washed, then placed in "coppers" made of wrought iron welded in one piece, and holding about 10 to 20 gallons, enclosed in outer jackets of the same material containing water which is kept well boiling. There are six coppers, about five feet high by three feet in diameter. The charge of each is about ½ cwt.; it is covered with soft water and well stirred with sticks for two hours, the scum and dross being occasionally skimmed off and thrown away as useless. At the end the size is ladled on to sieves, from which it runs into cooling vats, and is filled while moderately hot into clean tubs.

The liquor is clear and of a light-brown colour for the best XX quality, and darker for the common. The coolers or setting backs are of wood or zinc, and the liquid is not kept hot longer than it can be helped, as it is liable to turn sour.

Stephan remarks that "in the preparation of size, steam is usually let direct on to the materials, so that considerable dilution takes place". In his patent (English patent, 5,164, 1898) the size is placed in a boiler with double walls surrounded by steam "which does not come in contact with the size". The heating is done under pressure, and an arrangement is introduced for accurately measuring the size as it is passed into the troughs. A later patent (2,059, January, 1899) gives as an improvement "the employment of one or more suitable shaped discs . . . upon the shaft of the boiler . . . for the purpose of separating the various stages in the boiling of the sizing material, and causing the latter to pass from one stage to the other gradually, according to its development".

"Blue size," used by shoemakers as a first dressing for leather to fill up the pores and make an even foundation for blacking, was once an important article of the trade,

and several firms made it a specialty. It is still made, but is not so much in favour as formerly. It consisted of a size, the colour not being of much importance, dyed heavily with logwood, with the addition of a small proportion of alum or ferrous sulphate, to produce a bluish black. It has been replaced by "chemical dyes".

Mitscherlich patents a paper size made of *horn cuttings* dissolved in dilute alkali, with rosin added as long as it will dissolve. It is a transparent liquid which sets to a tough jelly when cold.

"Distemper" is whiting or sulphate of lime mixed with size and a pigment. The size is sometimes putrid, or becomes so in a damp place. Various antiseptics, such as salicylic acid, have been mixed with it, but it is generally sufficient if the size is good, and the drying not delayed.

"Concentrated size" is sold in packets for export.

Special Prepared Glues.

A large number of additions have been made to glue, many of them patented and highly recommended, but in most cases they have not answered the expectations of their inventors. It may be said generally that it is best, for nearly all purposes, to employ good glue without any admixture. The uselessness of powders has been already alluded to. The effect of chemicals is almost invariably to diminish the adhesive power or the consistence.

Mineral salts are liable to the following objections:—

1. Those which are efflorescent, like most salts of soda, creep up to the surface, and occasion a "bloom" or "frost" on the cakes or size, by forming a crust of small crystals. A similar fault attaches to sal ammoniac (ammonium chloride), which is frequently used to prevent frosting or cracking, after drying, in glues containing this substance: 2 to 5 parts glycerine is proposed to be added to 100 parts

boiling glue or size water, for every 15 parts of "sal ammoniac or its substitute" (English patent, 14,936, 1895).

2. Deliquescent salts, like chloride of calcium, tend to keep the glue damp and more susceptible to atmospheric conditions and to moulding. Chloride of calcium and zinc salts increase the adhesion to smooth non-porous surfaces, but at the same time diminish the drying power and tenacity. Horndam of Düsseldorff (German patent, 22,269, 1882) adds 8 to 10 per cent. of calcium or magnesium chloride, as an intended preservative, a purpose for which these salts do not act satisfactorily, and 30 per cent. to obtain a liquid preparation.

Many of these substances, such as sugar, etc., should be looked upon as weighting materials or adulterations.

Addition of Powders to Glue and Gelatine.

This practice has been described in chapter i., p. 17. Various objects have been assigned to it. In many varieties, some of them patented, white lead, oxide of zinc, and other powders are admixed, with the stated idea of forming a chemical compound with the glue, and thereby increasing its strength. That little or no combination does occur is proved by the fact that the insoluble powder can be extracted unaltered, with the exception of a small proportion which may have been dissolved by the acids or other substances contained in the glue. Nelson's "patent opaque gelatine" is whitened by the addition of a small quantity of finely divided carbonate of lime during the preparation, the effect being to give the jelly made from it the milky or opalescent appearance that is often preferred, besides, as in the Russian glue, conveying a distinctive trade character to the product. In the small quantity used, the addition is innocuous.

It may be laid down generally that the clearer a glue

appears, and the more free from clouds, streaks or spots, the more care has been exercised in its preparation, and the better is likely to be its quality.

Tanno-Gelatine.

The precipitate produced by tannin in a gelatine solution is sometimes supposed to be analogous to leather, but is quite different in properties. Hide after tanning is absolutely insoluble in water, but tanno-gelatine has a certain amount of solubility which depends on the kind of tannin, on the temperature, and on the other substances present. Moreover, leather is hard and consistent, whereas tanno-gelatine, until it has thoroughly set, is soft and adhesive. This character of tanno-gelatine has actually been made available in its use as a special cement, on account of its property of adhering firmly to leather. The *Papier Zeitung* (xviii., p. 2,618) gives the following formula for joints in leather driving belts :—

"Good hide glue and American isinglass in equal parts, after soaking for ten hours in water, are heated with pure tannin till the product becomes sticky. The ends should be roughened and the cement applied hot."

With the object of securing adhesion to metallic surfaces many mixtures have been proposed. Some of them contain sulphur, such as "Buller's Glue Compound," which is made from common glue, sulphur, and Paris white (English patent, 17,833, 1890).

Chrome Glue.

When glue solution is treated in the dark with soluble chromates, such as bichromate of potash or ammonia, or with chromic salts like chrome alum, no change takes place; but if exposed to sunlight, the glue is rendered insoluble in water. This property has been used in the "carbon process" of photography. After exposure to an image the

plate is soaked in water; the parts unaffected by light are dissolved, while those that have been acted on are left in relief. The picture, after hardening with alum, can be copied by electrotyping, impressed on soft metal (Woodburytype), or even printed from direct with lithographic ink (Collotype).

The reaction is also applied to the production of waterproof glue and coatings for fabrics.

An application of the compound of chromic acid with gelatine is suggested by Izard (*Comptes Rendus*, cxviii., p. 1,314). With a view to prevent the tarnishing of silvered surfaces, and especially the mirrors of astronomical telescopes, he coats them with a very fine film of bichromated gelatine, which is said to be extremely adherent, transparent, and lasting, and to furnish complete protection even under the action of gases like sulphuretted hydrogen. The process was successfully used on telescope mirrors at the Toulouse Observatory, and did not injure the definition.

Blasting "Gelatine".

The so-called gelatine explosives do not contain gelatine at all, but are made of various mixtures, whose basis is some form of soluble nitrocellulose or collodion cotton, therefore lie outside the scope of these articles. The name is derived from their horny consistence.

Flaked Gelatine.

With the object of promoting the easy solution of gelatine or glue, E. S. Spencer grinds it in a mill, sifts out the powder, and passes the coarser granules between smooth rollers, which may be gently warmed if necessary, till they are flattened out into thin flakes, which will then be readily soluble, and if well dried and carefully kept, are not affected by climate (English patent, 14,491, 1893).

Size, glue, or gelatin (Cannon, Lincoln, English patent, 10,596, 1891), are scented with various aromatic or antiseptic substances.

Coloured Papers.

A large quantity of the lighter glues were formerly employed in the manufacture of *coloured paper*, an industry that after 1870 received a great artificial impetus in Germany, with the usual result that the modern fast-working machines produced huge quantities, and caused a glut in the market, which led to the closing of about half the firms in this trade, with a corresponding cessation of the demand for the glue products. In 1896, according to *Handel's Museum*, there were in Germany fifty-five manufactories of coloured paper, many of which are in a precarious position, owing not only to fluctuations in prices, but to a general depression of the whole industry.

Formo-Gelatine.

Gelatine in aqueous solution is precipitated by formaldehyd, H.COH, or CH_2O, as a substance which on drying is a white powder, neutral, inodorous and insoluble in water and dilute chemical reagents; it is used as a dressing in surgery. In commerce, formaldehyde is met with in aqueous solution as "formalin," containing 40 per cent. of CH_2O. If 1 cc. of formalin be added to 200 cc. of a 5 per cent. gelatine solution, the latter is changed into a gelatinous mass, not melted by heat nor reduced by water. If a smaller quantity of the formalin is added (1 in 1000) the jelly is said to be meltable, but with a higher tenacity; when dried it becomes insoluble in warm water. Formalin in less proportion, though it does not prevent the dried gelatine from dissolving in warm water, is said to improve the "body" of the jelly and its keeping qualities, and also the tenacity of the glue. The following table is given of the properties

of a 5 per cent gelatine solution containing various proportions of the reagent formalin. The third column indicates the bearing weight of the jelly, exclusive of the weight of the disc (140 grammes) used as a sinker.

Percentage of formalin in the jelly.	Proportion of formaldehyde to 100 parts dry gelatine.	Bearing weight of the jelly in grammes.	Behaviour on warming.	Solubility after drying on a glass plate.
0	0	147	Liquefied	Soluble
0·005	0·4	148	,,	,,
·01	·08	163	,,	,,
·02	·16	173	,,	,,
·05	·40	192	,,	Insoluble
·10	·80	184	,,	,,
·20	1·6	553	Remains a jelly on warming	,,
·50	4·0	3090	,,	,,
·70	5·6	3800	,,	,,
1·0	8·0	4950	,,	,,
1·5	12·0	1520	,,	,,
2·0	16·0	1655	,,	,,
4·0	32·0	710	,,	,,
6·0	48·0	770	,,	,,
8·0	56·0	360	,,	,,
10·0	80·0	[?] 795	,,	,,
12·0	96·0	65	,,	,,

The results show that up to 1 per cent. of formalin the solidity of the jelly increases; above that it declines. Up to 0·02 per cent. (1 in 5,000) it re-dissolves in water after drying. Even with this small proportion the firmness of the jelly has been sensibly increased (147 to 173). With a 10 per cent. gelatine solution it had increased from 394 to 587. The English patent, 4,696, 1894, claims the addition of formalin during the manufacture of size and glue in such proportion that the product shall liquefy in warm water.

In examining commercial sheet gelatines for printers' and photographic use, we have often found small quantities of formalin present. It seems to improve the quality, a very small percentage increasing the tenacity, flexibility and keeping qualities, while not affecting the transparency or rendering the material acid. When applied to articles that

may be used as food, a strength of 1 in 50,000 in the final prepared product is not injurious to health, but should not be exceeded (Rideal & Foulerton, *Public Health*, May, 1899, p. 568).

Zimmermann (patent 8,391, 1897) applies dilute formaldehyde mixed with glycerine, vaseline, oil or yolks of eggs, with or without flour, to the surface of photographic films, " which are thereby rendered more pliable and not so hard as when the formalin is applied by itself ".

It will be gathered that formaldehyde in more than traces renders gelatine insoluble ; the product, moreover, is almost unaffected by water, is more or less hard and elastic, and, owing to the antiseptic properties of the formaldehyde, is nearly imperishable. In English patent 18,237, 1895, it is used for rendering glue and gelatine insoluble.

Preparation of Formo-Gelatin (Vloten, *Chem. Zeit.*, xx., 407).

Vloten prepares formo-gelatin in fine powder by precipitating a dilute warm solution of gelatin with formaldehyde slowly added with continual stirring. The mixture is then beaten with an egg whisk, and the precipitate of formo-gelatin is slowly produced as a scum similar to coagulated albumin, which can easily be removed from the liquid. The dried product is described as a " smooth powder which may be introduced into wounds without producing irritation ". It is called *Glutol*.

Unaltered Gelatin in Formo-Gelatin (Romyn, *Pharm. Weekblad*, xxxiii. [1], 1896).

The antiseptic value of a sample of formo-gelatin would be diminished by the presence of unaltered or free gelatin, and in this paper the following tests are proposed for its detection :—

(1) A portion of the sample to be tested is heated with

twenty times its weight of water for ten minutes at 100° C., and filtered while hot. If gelatin is present the filtrate will solidify when cooled.

(2) 0·5 gramme of the sample is treated with 6 cc. of dilute caustic soda, ammoniacal silver nitrate is then added, and in the presence of much unaltered gelatin no darkening will take place for some time, but fairly pure formo-gelatin will blacken in a few minutes.

With regard to the first test the author has noticed that pure "formo-gelatin is slowly decomposed by boiling water as the extract gives the biuret reaction".

Artificial Silk from Gelatin (Knecht, *Dyers' and Colours J.*, 14 [12], 252).

An interesting use for formo-gelatin is the production of Vanduara silk, which consists of extremely fine threads of gelatin treated with formaldehyde. A solution of the gelatin, containing any necessary colouring matter, at a constant temperature is drawn out into fine threads and, by means of an endless band, these threads slightly twisted are wound on to reels. The "fibre" is then subjected to the action of formaldehyde gas for some hours. Vanduara silk is claimed to be equal in appearance to the best net silk, but of course it is not so strong. The imitation silk is affected by moisture, becoming limp, but it regains its normal strength when dry. It is described as being insoluble in alcohol, ether, alkalies and acids, and burns like genuine silk. The cost of production is favourable, as the dyed article can be produced at less than 3s. 6d. per lb.

The Detection of Formaldehyde (Formalin) in Glue or Gelatin.

The following process for detecting the presence of formaldehyde in glue or gelatin has been found reliable in the

laboratory: A quantity of the sample, about 10 grammes, and an equal weight of water is placed in a Wurtz distilling flask and distilled by heating to 110° C. in an oil bath and passing steam into the liquid. The first 20 to 30 cc. of the distillate is collected and portions tested for the presence of formaldehyde by (1) Hehner's milk test, adding an equal volume of milk (free from formalin), and then concentrated sulphuric acid: a rose-purple colour at the junction will appear if $\frac{1}{10000}$ part of formaldehyde be present. (2) Carbolic acid test: One drop of dilute carbolic acid and then conc. H_2SO_4: a pink colour indicates formaldehyde. This test is exceedingly delicate. (3) Schiff's reagent. A dilute solution of magenta bleached by sulphurous acid has its tint restored by weak formaldehyde. But the test should be freshly prepared, is not very delicate or reliable, and is given by other aldehydes and by many substances. It is, however, useful as a positive and confirmatory test.

Liquid Glues.

A very large number of receipts, and even patents, are recorded for the production of a glue that shall remain permanently liquid, and not require dissolving or heating for use. It has long been known that the hardening of glue, or its gelatinisation, can be prevented by the addition of certain salts, or by the action of acids like nitric or acetic. But it will be easily understood that an agent which retains the glue permanently in a liquid form in the cold will also hinder its setting when it is used in the ordinary way, and in addition will probably reduce the ultimate tenacity, unless the agent used were a volatile one, like the spirituous solvents used for resinous cements. But glue and gelatine are not soluble to any extent in alcohol or ether, not at all in benzol, petroleum, and other hydrocarbons, and only form an emulsion with oils. For this and other reasons

the greater number of the recipes for the preparation of a glue that shall remain always liquid, after the manner of an ordinary gum bottle, are of no practical value.

One or two that have stood the test of long use and experience may be quoted:—

Acetic-gelatin. This is one of the most valuable of this class of cements, as it remains semi-liquid and is easily made quite fluid by warming; it is transparent and very tenacious, so that it is sold under many names, such as "giant," "diamond," "Hercules" cement, etc., for uniting glass and china, and for billiard tips. It can instantly be detected by the strong smell of acetic acid. Gelatin in fine threads is gently warmed and stirred with glacial acetic acid till dissolved.

"Diamond cement" is properly isinglass and gum ammoniacum dissolved in alcohol, and is practically waterproof. It is also used for glass and china.

If glue be dissolved in water, and one-fifth its weight of ordinary nitric acid be then added in small portions at a time, the solution will not gelatinise, but it still retains its adhesive powers. A very good liquid glue may be prepared by dissolving in a water bath 100 parts of glue in 250 parts of vinegar; 250 parts alcohol and 10 parts powdered alum are then added, and the whole heated for a quarter of an hour, when it is ready for use.

Another good liquid glue is made by heating for several hours on a water bath 12 parts glue, 32 parts water, 2 parts hydrochloric acid, and 3 parts zinc sulphate, the temperature not being allowed to rise above 180° F. This is called on the Continent "Knafft's glue": it will keep good for a long period, and is largely used for joining a great variety of materials, such as wood, horn and mother-of-pearl.

About 1895 a solution of chloral hydrate figured in a

large number of patents without much reason. It is expensive, and its efficiency as a bactericide and preservative is disappointing. When present to the extent of about 10 per cent., it causes the gelatine to remain permanently liquid, hence is an ingredient of many elaborate recipes for liquid glues.

An example of the extraordinary complexity of some of these recipes is seen in the following (English patent, 2,079, January, 1894) :—

"In 100 parts of water dissolve, successively,

"Chloral hydrate	2 parts,
Ammonium sulphocyanide	5 ,,
Boric acid	3 ,,
Zinc *chlorate*	0·5 ,,
Zinc sulphate	1 part,
Glue	450 parts,

stir frequently while mixing to prevent setting. The chloral hydrate and sulphocyanide produce the necessary degree of fluidity, while the desired tenacity and elasticity are produced by the boric acid and the zinc salts." It may be observed that if, as is usually the case, traces of iron were present in the glue or in the other ingredients, the liquid glue would acquire a more or less deep red colour, owing to the action of the sulphocyanide. The boric acid and zinc salts would act as antiseptics, but, like many other recipes of like nature, it is more than doubtful if the results would justify the trouble and expense.

Mineral glue (G. W. Bremner, London, English patent, 4,035, 1882). "Syrup of biphosphate of alumina, crystalline or mineral gum or syrup obtained from bauxite or any or all of them are heated to boiling with steam, and refined alumina added, as much as the stuff will absorb. Dissolved bone, ivory, horn, hair or ligamentous tissue is then added, and the whole boiled for several hours. A hard material that

will polish may be made by boiling this glue with plaster of Paris."

Liquid glue (Martens, Germany, English patent, 17,370, 1896). Glue made from leather parings is softened with water . . . 100 parts of glue to 150 of water . . . 10 parts of salicylic acid are added, and the mixture digested till clear. Oil of cloves is then added to the proportion of 1 gramme to each kilogramme of glue. The product, which remains liquid, is suggested as a gum substitute.

Elastic glue. Glue and glycerine in equal parts. Remains permanently elastic and soft.

Some examples may be given of glues made from other proteids.

Liquid casein glue (Bolder, Charlottenburg, English patent, 19,661, 1897). A mixture of casein, borax and water boiled for half an hour. It is a thick liquid of great adhesive power, and has long been used for certain purposes by joiners and bookbinders.

Waterproof glue (Gardner, English patent, 21,774, 1896) is a mixture of casein, albumin, blood, or gluten with the hydrates, carbonates, silicates, borates, or phosphates of the fixed alkalies.

Gluten glue is more of a paste than a glue. It is a very sour mixture of gluten and fermented flour, and has very little adhesive power (Wagner).

"Albumen glue" is a misnomer, as it contains neither glue nor albumen. It is partly decayed gluten from flour, washed with water and then heated to 15° or 20° C., when it ferments and becomes partly fluid (by bacterial action). It is then dried at 25° to 30° C., and "keeps any length of time in a dry place. Dissolved in twice its weight of water it can be used as glue for all purposes."

Puncture Fluids for Pneumatic Tyres.

A large demand has arisen for this special use. The requirements are somewhat exacting. It is necessary that the cement, carried in a small bottle, should be easy of application on an emergency, and should not be liable to deteriorate or become mouldy. It should remain liquid in the bottle, or should have the capacity of easy liquefaction by gentle warming, with the power of forming an elastic and tenacious plug. Patents are numerous. One class are based on india-rubber, gutta-percha, or gum resins, with spirituous or hydrocarbon solvents. These are not affected by water, but are said to injure the material of the tyres and to prevent a permanent repair; they are often also deficient in tenacity. Another section, though not quite waterproof, are excellent for temporary use; they are founded on glue with glycerine as a softener; for instance, glue, glycerine, water and chloroform (both the glycerine and the chloroform are antiseptics and render the preparation unalterable). Glue and glacial acetic acid is dangerous, although a strong cement, on account of the metal fittings. If too much glue is used in these recipes, the coat will be stiff and liable to crack.

A coat of Brunswick black will waterproof the mend for a time and prevent cracking. It must of course be allowed a little time to harden.

A "Glue Composition for Tyres, etc." (patent 18,864, 1896), called a "gelatinous resilient composition," is "an admixture of glue, sulphur, sulphate of barium, alum and collodion, with sulphuric, acetic, nitric and formic acids. It can be softened with glycerine."

Culinary Gelatine.

The value of gelatine as a food has given rise to much controversy, even to the extent of denying that it has any

value at all. On the other hand, popular opinion is apt to judge of the strength of a soup by its forming a stiff jelly when cold, and jellies, such as "calves' feet," are said to be very nourishing for invalids.[1] By physiological experiments it has been shown that "although in diet it will replace a certain amount of the true proteids,"—fibrin, albumin, and casein — "acting as a 'proteid-sparing' food, it cannot altogether take the place of proteids. Animals fed on gelatine instead of proteid waste rapidly" (Halliburton, *Essentials of Animal Physiology*, 1899).

Meat extracts, which are valued for their stimulant and not nutrient properties, are expected to contain only a small amount of gelatine. This is attained by digesting the comminuted fibre in cold water, when the gelatigenous tissue will not dissolve. Allen (*Commercial Organic Analysis*, vol. iv., 1898, p. 306) gives a table of analyses of commercial meat extracts, from which it appears that the gelatine varies from 0·25 to 5·50 per cent.: many of these have obviously been prepared by a hot process. The objection to gelatine in these preparations is that it gives a spurious solidity and conceals an extra amount of water.

For culinary purposes the form in thin sheets is commonly placed under the crust of raised pies, etc., to melt down gradually. For soups a number of varieties are made—thread, cut, and fancy gelatines; some are nearly white, and bear a close resemblance to isinglass; in fact they are sometimes sold as "patent Isinglass".

[1] I have found in three "Invalid Jellies" in the market the following amounts of gelatin: Brand's, 5·15; Mason's, 5·48; Maynard's, 4·11 per cent.

An examination in our laboratory of a number of commercial kinds gave results as follows :—

Characters of the 10 *per cent. Jellies.*

	Ashworth's				Cox's.	Nelson's.	Swinbourne's.
	No. 1.[1]	No. 2.	No. 3.	No. 4.			
Colour . . .	pale brown	pale brown	light brown	pale brown	pale brown	pale brown	light brown
Appearance . .	cloudy	opalescent	cloudy	cloudy	nearly clear	opaque	semi-opaque
Insoluble matter .	trace of brown	trace of brownish	trace of dark stringy	trace of dark stringy	minute trace of sandy	white—mainly chalk	white—partly soluble in HCl.
Odour (hot) . .	slightly gluey	none	none	none	faintly gluey	none	none
,, (cold) .	none	none	none	none	none	none	none
Liquefying pt. C°.	19	22	28·5	28	24	28	26
,, ,, F°.	66·2	71·6	83·2	82·4	75·2	82·4	78·8
Units of water absorbed—1 hr. .	7·05	7·46	8·54	7·65	6·08	5·69	5·89
,, ,, 48 hrs.	10·65	10·76	10·80	9·30	12·66	9·43	8·89
Consistence cold .	firm	firm	very firm	very firm	firm	firm	firm
Reaction . .	faintly alkaline	faintly alkaline	very faintly alkaline	very faintly alkaline	faintly alkaline	distinctly alkaline	slightly alkaline

Composition of the Original Gelatins per cent.

Water . . .	19·21	18·15	17·36	17·92	18·88	17·10	18·23
Ash . . .	0·95	1·19	0·98	0·80	1·51	3·80	1·72
Organic Matter .	79·84	80·66	81·66	81·28	79·61	79·10	80·05
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

Nelson's Patent Gelatine is rendered opaque by a small quantity of chalk. It is stated to be prepared by washing skin parings, etc., and digesting them in dilute sodium hydroxide solution for ten days. They are kept at a temperature of 70° F. in an air-tight vessel, and afterwards

[1] No. 1 was found to be "free from chondrin; suitable for culinary, but rather soft for photographic use, unless mixed with a 'hard' gelatin".

For ordinary photographic emulsions Abney recommends a mixture of "hard" and "soft" gelatins in proportions dependent on the weather, "a good mixture being 1 part hard to 3 soft".

thoroughly washed in cold water. They are then bleached by sulphurous acid, as described in Chapter II., again washed and converted into gelatine by heating with water.

Swinbourne's Gelatine (English patent, 9,033 and 11,975, 1888).

Hides, skins, or glue-pieces free from hair, reduced to shavings or slices, soaked five or six hours in cold water, then the water changed, and so on for some days until no smell or taste. If intended for soup, the shavings are merely dried, and are then ready. If for gelatin, they are heated with water, not above boiling, strained through the filter cloths, and run on to slate or other material to dry. They cut up similarly cod-sounds or other fishy matters.

Bones yield excellent culinary gelatine, clear, transparent, inodorous, and nearly tasteless.

ISINGLASS

is not a gelatin, but a *collagen* which is very easily converted into gelatine by heating with water. It is properly prepared by slicing and drying carefully the swimming bladder or "sound" of the sturgeon (*Acipenser vulgaris*), but many other fishes will yield an article little inferior. The commercial article occurs in fine yellowish-white threads, translucent and tenacious, free from odour, and having a very faint fishy taste.

It is distinguished from gelatine imitations by soaking in warm water and examining under the microscope, when true isinglass will show a network of long curling fibres, while gelatine will be simply hyaline. In hot water isinglass dissolves almost entirely, and gives a very firm jelly on cooling, strongest in the "Russian" variety, from the sturgeon.

"Brazilian" or "Cayenne" isinglass, from the fish *Silurus Parkeri*, is met with in sheets an inch or more in thickness.

"Rat's-tail" isinglass, from the sound of the cod, hake and other fishes, is opaque and incompletely soluble.

For soups, jellies, etc., a good quality gelatine is practically equal to the more expensive isinglass, and is frequently sold as such: it takes rather longer to prepare.

F. Prollius (Dingler's *Polyt. J.*, ccxlix., 425) gives the following determinations in various foreign samples. For the viscosity, 1 part of the specimen was dissolved in 90 parts water:—

	Water	Ash.	Insoluble matter.	Time required for solution to run out.
	Per cent.	Per cent.	Per cent.	Seconds.
Astrachan, from Schmidt & Dihlmann, Stuttgart	16·0	0·20	2·8	507
Astrachan, from a collection	18·0	0·37	0·7	485
Astrachan, fine iridescent Russian quality, Tubingen collection	17·0	1·20	1·0	500
Astrachan, Russian, from Gehe of Dresden	19·0	0·80	3·0	491
Astrachan, in laminae from Gehe	19·0	0·50	0·4	480
Astrachan, in threads, known as Hamburg threads	17·0	0·40	1·3	477
Hamburg isinglass	19·0	1·30	2·3	470
Another quality	19·0	0·13	5·2	—
Rolled northern, fish bladder	1·5	3·20	10·8	467
Icelandish bladder	17·0	0·60	21·6	463
Indian isinglass	18·0	0·78	8·6	437
Yellow, quality unknown	17·0	2·30	15·6	360

Finings.

The use of isinglass, especially the commoner kinds, for clarification, is due almost entirely to the fine fibres already mentioned, which entangle and carry down suspended matter, therefore in this case gelatine will not act as a substitute. For beer the finings are supplied ready-made, and consist of Brazilian isinglass dissolved in sour beer with a variable addition of sulphurous acid or calcium bisulphite. They are often very foul in character. Inasmuch as the addition of "finings" to liquors has often been made a

cloak for adulteration, the maximum amount that may be added, and its nature, is in most countries prescribed by the excise. On a large scale the isinglass after soaking is reduced to a fine state of suspension in the water or other liquid by pressing with revolving brushes through sieves.

Isinglass Substitute ("Isinglassine").

The gelatinous material from calves' feet and other sources is reduced by machinery to a pliable homogeneous mass, rolled out into sheets, dried, pressed and shredded; each round is cut into about 125,000 shreds or staples.

Many lichens and seaweeds give a jelly on boiling which is used in food and sometimes in medicine. The substances causing the gelatinising property are mostly non-nitrogenous and are related to cellulose.

Irish Moss (*Chondrus crispus*) contains "Carrageenin," allied to pectin. It has been employed as a substitute for isinglass, as a size, for thickening colours in calico printing and in stiffening silk.

Gelose, from *Gelidium corneum*, or Chinese moss, is met with in commerce in long thin threads called "Japanese isinglass," but although it is said to have ten times the gelatinising power of the real article, it is not a suitable substitute since the melting point of the jelly is above the temperature of the mouth. (Allen.) Agar-agar is a similar substance sold in long hollow prisms, and much used for high temperature cultures in bacteriology instead of gelatine plates, which would become liquid above 26° C.

Algin or alginic acid is a gelatinous body first isolated by Stanford from Laminaria and other seaweeds. Although nitrogenous, it is not a proteid, as will be seen by comparing the formulæ.

Gelatin (Schutzenberger) $C_{76}H_{124}N_{24}O_{29}$.

Algin, $C_{76}H_{80}N_2O_{22}$.

Medicinal and Other Uses.

Gelatine is thus mentioned in the *British Pharmacopœia* of 1898 :—

"*Gelatinum*, Gelatin.—The air-dried product of the action of boiling water on such animal tissues as skin, tendons, ligaments and bones.

"*Characters and Tests.*—In translucent and almost colourless sheets or shreds, a solution in 50 parts of hot *water* is inodorous, and solidifies to a jelly on cooling. Gelatin is insoluble in *alcohol* (90 per cent.) and *ether*. It dissolves in *acetic acid*. Its aqueous solution yields a precipitate with *solution of tannic acid*, but not with solutions of other acids, nor with *solutions of* alum, lead acetate, or test-solution of ferric chloride."

The definition would seem to exclude fish gelatine. The last paragraph demands the absence of chondrin. Gelatin is made official for the preparation of glycerine suppositories.

The appendix prescribes :—

"*Solution of Isinglass.*

"Isinglass, in shreds, 4 grammes. Distilled water, warm, sufficient to produce 200 cubic centimetres. Mix, and digest for half an hour on a water bath with repeated shaking, and filter through clean moistened tow. Solution of isinglass must be recently prepared."

It is used for testing the freedom of gallic acid from tannic. Ordinary gelatine answers equally well.

Two unofficial preparations are :—

Vinum Xericum detannatum, and *Vinum Aurantii* ditto : detannated sherry and orange wines. Half an ounce of gelatine, cut small, is macerated with one gallon of the wines for fourteen days, and decanted clear from the insoluble tanno-gelatine. The object is for preparing various medicated wines with drugs that would be precipated by tannin.

"Lamellæ" are discs of gelatin with some glycerin, weighing $\frac{1}{50}$ to $\frac{1}{30}$ grain, and containing a minute dose of a powerful alkaloid, to be dissolved in water for ophthalmic and hypodermic use. Four kinds are specified in the British Pharmacopœia.

"Glycerin jelly" is a solution of gelatin in glycerin used for mounting microscopic sections. A semi-solid mixture of the same is official as *Glycerin suppositories;* also in the Throat Hospital pharmacopœia in two different consistencies as *Gelato-glycerin* and *Glyco-gelatin*, the former used for nasal bougies, the latter for medicated lozenges. Glycerin jelly is also used for the hands.

Gelatin capsules, for nauseous drugs, and gelatin-coated pills are well known.

Minor uses of gelatin are in confectionery, and in coloured sheets for toys. Deeply coloured sheets of this kind were successfully introduced some years ago in London for colouring theatrical limelights, and were found when mounted in frames to be much lighter, less expensive and fragile, and more easily renewed than the glass plates previously used: they are not much affected by the heat, especially if a cell of alum solution is interposed, as is done in the cinematograph.

Use of Gelatin in Bacteriology.

Of late years a considerable demand has arisen for the finest qualities of gelatin for purposes of bacteriological research. The gelatin employed in this work must be quite clear and bright, any opalescence such as is present in Nelson's being very objectionable, it must also be fairly neutral, and especially of high gelatinising power. Hitherto this demand has been supplied almost entirely from the Continent, but latterly English firms have turned out gelatin quite equal if not superior to foreign makers, for this purpose.

As already pointed out in describing its manufacture, most bacteria, under certain conditions, find gelatin a medium for rapid and luxuriant growth. For bacteriological work the gelatin obtained in the form of sheets or thin strips is made up to a 10 to 20 per cent. solution with meat broth, and this nutrient jelly, which is obtained by clarification with albumen perfectly clear and bright, forms a most useful medium for the cultivation of micro-organisms; it allows any growths to be easily examined under the microscope, and the jelly can be remelted, and moulded to any required shape, without the danger of killing the bacteria by overheating. Moreover, it affords an important distinction between various species as to whether they are capable of permanently liquefying the gelatin or not.

CHAPTER V.

GLUE TESTING.

MUCH controversy, especially in Germany, has centred on the large number of methods that have been proposed for glue testing, and there is no doubt that difficulties arise in the interpretation of results, and in obtaining absolute measures, or figures that shall be comparable between different observers. Therefore the necessity for agreeing upon standard methods of working, or at least of stating in each case the exact details of procedure. Systematic tests, however, are of use to manufacturers in controlling their processes, and to users in avoiding loss and mistakes in purchasing, owing to the fancy prices and misleading names and descriptions frequently put forward.

Julius Fels (*Chem. Zeitung*, xxi., Nos. 8 and 9, 1897) gives the following list of methods, to which we annex his criticisms :—

A. *Chemical Methods.*

1. Gräger. Dingler's *Polyt. J.*, 1852, 126, 124. *Tannin Titration.* "The tanno-gelatine is of uncertain constitution."

2. Noffat. Wagner's *Jahresb.*, 1867, 672. *Nitrogen by soda lime.* "Other nitrogenous compounds are present."

3. C. Stelling. *Chem. Zeit.*, 1896, xx., 461. *Estimation of matters not glue* (after pptn. by tannin or by alcohol). "Inaccurate." (See F. Gautier, *Zeit. f. Anal. Chem.*, xxxiii., 4.)

B. *Physical Methods.*

4. Schattenmann. Dingler's *Polyt. J.*, 1845, xcvi., 115. Absorption of cold water on soaking. "Uncertain."

5. Cadet. Absorption in damp air. "Unreliable."

6. Lipowitz. *Neue Chem.-techn. Unters.*, Berlin, 1861, 37-42. Consistency and bearing weight of jelly. "Correct as a comparative method."

7. Weidenbusch. Dingler's *Polyt. J.*, 1859, 152, 204. Breaking strain of a rod made of glue and plaster of Paris. "Uncertain."

8. Artillerie Werkstätte Spandau. Weight required to separate two pieces of wood glued together. "Depends on time."

9. Fels himself recommends determining the viscosity of a 15 per cent. jelly by Engler's viscosimeter (*Journ. Soc. Chem. Ind.*, 1890, p. 654).

CHEMICAL EXAMINATION.

The determination of water and ash is necessary in order to render the other results comparable, and to assist in detecting adulteration. Ordinary glue of good quality contains from 12 to 18 per cent. of water; a low result generally is a bad sign, as overdrying is known to injure the tenacity, while a high percentage diminishes the keeping qualities, besides adding spuriously to the weight. The ash is usually from 1·5 to 3 per cent., and its amount does not discriminate between hide and bone glues. It will obviously be much higher if mineral fillings have been added or the source is impure. The qualitative examination of the ash on the other hand gives a clue to the origin, as the ash of bone-glue fuses, its solution is neutral, and it contains both phosphoric acid and chlorine, whereas ash of hide-glue does not fuse, because it contains lime; it is alkaline, and nearly or quite free from chloride or phosphate.

After breaking in small pieces, a sufficient quantity of the glue is either reduced to shavings in a machine, or is pounded in a mortar, the pestle passing through a perforated cardboard guard to prevent scattering. One or two grammes of the coarse powder weighed in a platinum dish are dried first in the water oven, then at 110° to 115° C. till the weight is constant. The loss is water plus a small quantity of other volatile matter. Cautious incineration at a low temperature gives the ash, which should dissolve almost completely on warming with dilute nitric acid, the solution being tested for chlorides and phosphates, and also for other substances if necessary. The presence of more than a small amount of salt deteriorates the quality and appearance of glue. An excess of chlorine may also indicate that chloride of lime has been used as a bleacher in the manufacture. Various earthy powders added to glue during manufacture will be found in the ash. White lead, lead sulphate, zinc oxide, barium sulphate, and even lead chromate have been used.

Reaction of the Glue.

If a glue is acid, about 10 grammes of the powder are dissolved in warm water, and divided into two portions; in one the *total acidity* is estimated by standard alkali, the other is evaporated on the water bath, redissolved, and the *fixed acidity* determined. The difference gives the *volatile acids.* As the nature and amount of the acids present in glue is often of importance, a closer examination may be made by distilling 30 grammes in 100 cubic centimetres of water by a current of steam, when the volatile acids will pass over. The distillate should be examined for free sulphurous acid, as it is sometimes present, having been used for preserving or bleaching, and its presence is generally objectionable. In leather-glues the volatile acids are about 0·02 per cent., in bone-glues from 0 to 0·5; the higher amounts, with a smell

of acetic or butyric acid, indicate that the jelly has been soured during the manufacture, and that the glue is unsuitable for many purposes. Kissling states that glue solutions which do not alter litmus may yet react with phenolphthalein, "probably owing to an organic acid". He estimated this with soda, but did not ascertain its nature.

Any undue quantity of acid can be roughly detected by the taste. Glues may be *alkaline* from the addition of excess of lime in the manufacture to correct the sourness of the jelly. A large manufacturer informs us that "a little acid or a little lime does not hurt, though it is much better neutral. We find that our customers prefer a glue that shows a little lime, rather than any acid, although an acid-made glue is not nearly so apt to decompose as a lime-made glue." Most of the bacteria which cause changes in glue thrive better in alkaline solutions, and are actually antagonised by acids. For uses, where colours are concerned, the glue must be neutral to litmus; for adhesive uses this does not matter, unless the alkalinity or acidity is due to defective preparation. When the solution of glue in hot water rises higher than 100° C., it begins to sour, and loses to some extent its property of forming a jelly. Sulphurous acid and sulphites are said to cause light patches on dyed wool. Kalmann states that the amount of sulphite can be determined, after titration of the acidity with soda and phenolphthalein, by means of iodine solution and starch, the organic matter not interfering. He mentions that for woollen manufacturers the glue must not exceed—free acid equal to 1 per cent. Na_2O, SO_2 0·5, ash 3, water 15 per cent.

Insoluble Matters.

As extraction with water, filtration and weighing are somewhat tedious, a comparative result may be obtained by dissolving 30 grammes, making up to 1 litre in a

graduated cylinder with hot water, allowing to stand in a warm place for twelve hours, then noting the volume of the deposit as "foreign matter," stating the quantities taken. The solution may be used for other tests.

Determination of Gelatine.

The organic matters of glue are very complex. Among the nitrogenous matters to be found in it there are probably several varieties of gelatine and chondrine, as analyses of these substances, presumably pure, show differences in elementary composition, in addition to the variations in physical properties. Products of change, such as albumoses and peptones are usually present, with small quantities of bases, sugars, and ill-defined bodies. For this reason the content of nitrogen and the various processes of precipitation by tannin, etc., yield results which have little relation to the commercial value. Gelatine has a greater power of adhesion and gelatinisation than chondrine; the latter, however, is largely employed for size.

The Bisler-Beumat method of tannin titration is briefly as follows: Two solutions are prepared: (*a*) 10 grammes of pure tannin to the litre; (*b*) 10 grammes of pure isinglass and 20 grammes of alum to the litre. The latter is added to a measured quantity of the former till no further precipitate is produced; the volume used is read off on the burette. The same volume of tannin is then precipitated by a 1 per cent. solution of the glue; the relation between the volumes of glue solution and of isinglass gives the ratio of the glue to the sample of isinglass taken as a standard. Different specimens of isinglass and of tannin themselves show different ratios of precipitation; 42·7 parts of gelatine are said to be equivalent to 57·3 of tannin, but the precipitate is somewhat variable in solubility and composition. Another process is to add tannin in excess, and estimate the amount

of tannin left in solution by running in standard permanganate as long as it is decolorised. The proteids can be more exactly precipitated by chlorine (Rideal & Stewart, *Analyst*, September, 1897), or by bromine (Allen & Searle, *ibid.*, October, 1897).

The presence of chondrine reduces the value of gelatine, especially for photographic emulsions. It may be detected by adding a concentrated solution of chrome alum to the glue or gelatine, dissolved in 10 parts of boiling water; if any injurious quantity of chondrine be present, the liquid will set while hot.

Fat is very objectionable in glue, and for many purposes must be entirely absent. It renders the hot solution turbid, and on standing collects at the top as a greasy film, which may be removed by ether when the jelly cools. A manufacturer's "grease test" is described as follows: "To a solution of glue add a little lampblack or Turkish red; thoroughly mix with a brush, and paint it on some pieces of paper; if there is an abundance of grease, it will show by little round, white, smooth surfaces on the red or black paint. Specially required for the paper trade and some others."

To determine the fat exactly, 20 grammes of the broken glue are treated with 50 cc. of water and 5 cc. of hydrochloric acid (to decompose any soaps). When the glue has dissolved, sufficient calcium sulphate or clean sand is added to take up the water, and the mass is dried for some hours at 105° C., and carefully granulated. It is then extracted with ether in a Soxhlet apparatus for five to six hours, and the extract dried and weighed. Kissling uses petroleum ether for extracting the fat.

Stelling's process for determining "matters not glue" consists in adding to a solution of 1 part glue to 4 parts of water alcohol of 96 per cent. in small quantities at a time, constantly stirring. Kissling says of this method: "We take 15 parts of glue and 60 parts of water, and make up

to 250 cc. with alcohol, then determine the proportion of non-gluey matter present by evaporating down an aliquot part of the alcohol solution, previously filtered, and weighing the residue. The process is thus based on the supposition that alcohol of about 72 per cent. in volume leaves the gelatine intact, while it dissolves the products of decomposition, considered as non-gluey material."

But gelatine is not entirely insoluble in alcohol of 72 per cent., inasmuch as, on evaporating down the filtered alcoholic solution, we obtain a residue consisting principally of gelatine and possessing a strong adhesive power, almost equal to that of the original glue employed.

Nevertheless it cannot be denied that Stelling's process has a certain value—very small, it is true—for the valuation of glues; since, when we have to deal with products of a superior quality, the substances soluble in alcohol are in quantities much smaller than are present in ordinary glues.

Saponification Process.

W. Fahrion (*Zeit. Angeh. Chem.*, 1898, p. 529) evaporates 3 to 5 grammes with 15 to 25 cc. of an 8 per cent. solution of alcoholic soda to dryness, washes with hot water into a separating funnel, acidifies with HCl, cools and extracts with ether. The aqueous layer retains "solid oxyacids," which are afterwards extracted by warm alcohol. The ether dissolves unsaponifiable matter, fatty acids, and "fluid oxyacids"; the latter are insoluble in petroleum ether, the two former are separated by aqueous soda.

He gives the following analyses of glue and glue-yielding substances :—

	Moisture.	Mineral Matter.	Unsaponifiable Matter.	Fatty Acids.	Oxy-acids— Solid.	Oxy-acids— Liquid.	Proteids.
Very pure white glue	13·74	1·80	0·49	0·08	0·04	0·27	85·58
Animal hide powder	19·15	0·25	0·72	0·18	0·08	0·37	79·25
Hide dressings . .	11·23	10·06	9·74	0·99	0·46	1·01	66·51
Horn of sheep . .	9·09	1·00	0·68	1·03	0·29	1·49	87·62
Bony part of sheep .	10·00	53·87	4·81	4·23	0·19	1·52	25·38

Kissling considers that the above process "may possibly throw light on the constitution of gelatine, but that it is not suitable for commercial work".

Determination of Nitrogen Content.

The determination of the amount of nitrogen in raw materials after washing, and in gelatines, is of great value. It is accomplished most easily by the Kjeldahl process.

From ¼ to ½ gramme of the material in small pieces is accurately weighed and is placed in a "Jena glass" flask with long neck, supported on a concave piece of wire gauze over a Bunsen burner. A sand bath is not advisable, on account of the slowness, and danger of bumping. The flasks are preferably arranged in series in a slanting position on rails of iron rod in a good stink-cupboard: 20 cc. of sulphuric acid free from nitrogen, about 1 gramme of potassium sulphate (to raise the boiling-point), and a small globule of mercury are added. On applying heat at first there is danger of frothing or spurting, therefore the operation has to be carefully watched; after a time it proceeds without attention if the heat is regulated. As soon as the liquid is only faintly coloured, it is allowed to become cold, then water is added cautiously, and it is washed into a Jena flask to a dilution of 600 cc., cooled, a piece of clean litmus paper added, then 50 per cent. soda solution, free from ammonia, till the litmus is blued, finally 1 or 2 cc. of pure strong sodium sulphide solution to precipitate the mercury and prevent its retaining ammonia, and three pieces of ignited pumice. Without delay the flask is connected with a condenser, and the contents distilled into a U-tube, containing 50 cc. of decinormal sulphuric acid, accurately measured, until 250 cc. has come over. This is then titrated with standard soda, using methyl-orange as indicator. The loss of acidity, due to neutralisation by

ammonia, is thus obtained. Each cc. = ·0014 gramme nitrogen. Multiplying by 5·56[1] gives very closely the amount of gelatine, if other nitrogenous substances are not present.

V. Schroeder and Paessler (Dingler's *Polyt. J.*, 287, pp. 258, 283, 300) give as the content of nitrogen in various purified skins dried at 100° C. :—

Ox, calf, horse, pig, camel . .	17·8 per cent.
Goat and deer	17·4 ,,
Sheep and dog	17·0 ,,
Cat	17·1 ,,
Gelatine	18·1 ,,

It is very difficult to obtain gelatin pure and dry: Allen gives 17·9 as the percentage of nitrogen, I have found up to 18·2. But these differences are small when compared with the quantity found in other proteids, which is much lower, for example :—

Albumen	15·7 per cent.
Elastin	16·7 ,,
Fibrin	16·9 ,,
Paraglobulin (from blood) . .	15·85 ,,
Keratin	16·8 ,,

On the other hand, many decomposition products contain a much higher percentage of nitrogen than gelatin.

For commercial purposes the total nitrogen multiplied by 5·56 is put down as gelatin or "real glue". Adding the ash and moisture and subtracting from 100 gives a remainder of "other organic matter," which does not add to the strength. As examples of analyses on these lines

[1] This factor for gelatine is derived from the following figures obtained by different observers :—

	Per cent. N.	Factor.
Allen	17·9	5·59
Chittenden	17·97	5·57
Schroeder & Paessler . .	18·1	5·52
Rideal	18·0	5·57

the results obtained in our laboratory with four samples of high-grade gelatins are appended, and it will be noticed that the figures for "other organic matter" are very small, amounting in only one instance to over 1 per cent.:—

	Nelson's. A.	Nelson's. B.	Coignet's "Extra".	Swiss "Gold Label".
Water	18·96	17·10	19·41	17·84
Ash	4·19	3·80	1·50	1·47
Gelatin (total N) (x 5·56) . .	76·73	78·26	78·34	79·67
Non-nitrogenous organic matter	0·12	0·84	0·75	1·02
	100·00	100·00	100·00	100·00

Adulterations and Admixtures.

It has been already mentioned that mineral impurities will be found in the ash.

If the figure obtained for "other matters," as described in the last section, be unduly high, gum, dextrin, sugar, or glycerin may be suspected. When a 25 per cent. solution of the material is precipitated by absolute alcohol, the sugar and glycerin remain dissolved, and are left on evaporation as a sweet residue, in which the sugar may be found and determined by Fehling's test, the difference being approximately the glycerin. The matter insoluble in alcohol is boiled with dilute (1 per cent.) HCl, whereby gum and dextrine are inverted, and then, after alkalising, will reduce Fehling's test on heating.

Evers points out (*Chem. Zeit.*, 1899, 23 [31], 333) that wheat gluten closely resembles animal glue in its behaviour to reagents, but yields with a *small quantity* of sodium chloride or magnesium sulphate a voluminous precipitate, whereas pure glue remains clear.

Gelatine is sometimes itself used to adulterate other substances. A small quantity added to chocolate has been found to raise considerably the percentage of water that can be introduced. [Onfroy describes a process for its detection :

J. Soc. Chem. Ind., 1898, 802.] For the same reason it is often added in undue quantity to meat extracts. When used for weighing or stiffening fabrics, its amount may be ascertained by extracting with hot water and determining the nitrogen, confirming also by other tests.

Physical Tests.

Glue should not become damp in ordinary air, or it is liable to turn mouldy. This fault would indicate impurity or adulteration. The author has met with a few instances of weighting with coarse sugar, molasses or dextrine, in which this peculiarity was conspicuous.

1. The appearance, hardness, and manner of breaking furnish an idea of value which can be learnt by practice. A splintery fracture shows that the glue is not well boiled. Glue from bones presents a milky appearance, due to a little calcium phosphate. Glue without gloss, very much warped, and of a very dark colour, may be excellent in adhesiveness and tenacity.

2. *Drying and Keeping Qualities.*—About 10 cubic centimetres of a 20 per cent. solution are placed on a watch glass in a cool dry place, protected from dust, and observed for several days in comparison with a standard sample.

3. *Smell.*—Varies very much. Leather glue smells least. Some do not smell when cold, but the hot solution is unpleasant. This property is of importance for some uses. Standard glues may be kept in powder for comparison; they retain their smell for years in closed bottles. The smell very often indicates the source: hide glue, pig's-foot, bone and fish glue all have a characteristic odour.

4. *Behaviour with Cold Water.*—Schattenmann in 1845 proposed the absorption of cold water on soaking. Ten grammes of the sample in small pieces are placed in a weighed beaker, aud covered with 200 cc. of water, and

kept covered at 60° F. for forty-eight hours. The water is then poured off and the remainder weighed. According to my experience, good glues will absorb about five and a half to six times their weight of cold water, and still exhibit a firm jelly. Some will even absorb eight to ten times their weight and still remain fairly firm. The more consistent and elastic in this state the greater the adhesive power, and the more water it absorbs the more economical in use. Bad glues will often become slimy and fluid in less than forty-eight hours. The water poured off should be free from putrid odour, and contain little in solution. The test is specially applicable to bone glue; that from animal offal does not show the same behaviour.

Kissling soaks 100 grammes of the glue (apparently unbroken), supported on fine wire gauze, in cold water, and weighs at intervals of twenty-four hours, draining fifteen minutes before each weighing. In forty-eight hours he obtains numbers from 221 grammes to 332 grammes of water absorbed, his highest figure being 723 grammes in 216 hours. This method seems inferior to the above. Still less can Cadet's method, absorption in damp air, be recommended.

Schlossmann (*Papier Zeitung*, xvii., 2484) takes strips of equal size (50 × 150 mm.), including a standard glue which is found to work well for the special purpose, makes two perforations with a hot rod, and suspends them by the upper perforation in graduated cylinders holding a litre of cold water, attaching a weight to the lower hole. At the end of every twelve hours, as long as the strips will hold together, they are carefully lifted and drained, and the volume of remaining liquid and its character observed. "Good parchment and leather glues should be firm and sweet after two days in summer and four in winter."

In America the absorption is usually stated in ounces per

pound of dry glue. Thus "a water test of 96" means that 1 lb. of glue has absorbed in twelve hours 96 ozs. of ice-cold water, equal to six times its weight. It is said, on the other hand, that with heavily evaporated glues, or those cut in very thick sheets, the water-test results are unreliable.

5. *Lipowitz' Method*, 1861 : *Consistency and Bearing Weight of the Jelly.*—A 10 per cent. hot solution (the jelly from the 10 grammes in the preceding process, No. 4, could be made up to 100 grammes with hot water) is allowed to stand twelve hours at 18° C. in a cylinder of uniform width to gelatinise. A metal rod is soldered to the centre of the interior of a small tin cup, and is supported vertically by passing loosely through holes in two horizontal plates, one of which forms the cover of the cylinder, the other being fixed a little higher. The upper end of the rod carries a funnel, which can be loaded with fine shot. The cup is allowed to rest on the jelly, and the funnel is loaded until it sinks a certain distance into the jelly; the weight of shot then gives the Lipowitz number. The cylinder should be surrounded by a water jacket to maintain a definite temperature. The result is also affected by the diameter of the cylinder and of the cup. Lipowitz gives the following figures :—

Variety of Glue.	Weight required to force the saucer down. lb.
Breslau	3·74
Russian	3·18
Cologne	2·67
Muhlhausen I.	1·60
Nördlingen	1·59
Muhlhausen II.	0·85

The table from which the above figures are taken also contains the following: 1. Water 9 to 21. 2. The percentage of gelatine by tannin is in the same proportion as the water absorbed. 3. The weight supported by the jelly corresponds

neither with the absorption nor content of gelatine, nor with the price. (A reason for this has been given in the first chapter.)

A commercial form of the above, called the "shot-test," is made by cooling the 10 per cent. solution in an ice-box for three or four hours till firmly set. A tube or small beaker is placed on the jelly and loaded with shot till it sinks. By this method I have found that a 10 per cent. jelly will bear a weight, ranging in different glues from 64 to 12 grammes, in bad cases falling to 0, the glue being liquid. Kissling ascertains how many seconds are taken by a glass, a zinc,

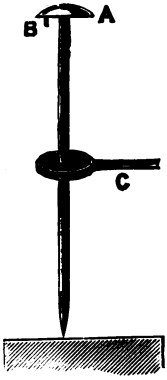

FIG. 12. Kissling's Consistency Apparatus.

and a brass rod, weighing respectively 50, 100, and 150 grammes, and 8 to 10 mm. in diameter, to sink to a zero mark into a jelly.

The apparatus he uses was originally devised for testing lubricating greases.

The height of the support is so adjusted that the distance of the bottom of the pin B from the guide C is 100 millimetres.

He soaks 100 grammes of the sample in 300 cc. of water overnight, warms for a short time next day till fluid, then maintains at 20° C. for four hours to set. "When the brass

rod takes 850 seconds, or longer, to sink, the consistency is 100; while, if the glass rod sinks in less than one second, the consistency is 0." He gives the following examples :—

	Price in marks per 100 kilos.	Gelatinising power.
Leather glue, 1 . . .	90	50
„ „ 2 . . .	80	25
„ „ 3 . . .	75	100
„ „ 4 . . .	70	100
Mixed glue, 5 . . .	55	0
„ „ 6 . . .	55	3
Bone glue, 7 . . .	50	5
„ „ 8 . . .	45	2
„ „ 9 . . .	43	22
„ „ 10 . . .	41	24

He finds that skin-glues have a higher consistency of jelly, less odour, impurity, and volatile acid than bone glue, the water, ash, breaking strain, and absorption of water being about the same in both classes. But, like other observers, he can find no definite or constant relation between these factors and the price.

I may here give a few notes from my own determinations of the consistency of jellies. As determined by the "shot test," the bearing weight is not the same as Kissling's "consistency" or "gelatinising power". The former is affected considerably by the skin which always forms to a greater or less extent on the surface of the jelly. This can be avoided by slicing off, or by casting in a cylinder with false bottom and inverting, but it will be found that the jelly yields considerably at first by its elasticity *without breaking*, and that if the weight be lifted the surface will recover its flatness. The point should be taken when the meniscus of depression suddenly rises, showing that the sinker has penetrated.

I find it more convenient to employ, instead of a pointed rod, a round-ended thin glass tube which can be weighted with mercury or shot, and to graduate the containing vessel in millimetres. It will be found that as the weight is

gradually increased, the tube will penetrate the jelly a certain distance and then stop; with careful further increase it will advance further and again stop, and so on till a weight is reached which carries it to the required distance (100 mm. in Kissling's method). These positions of equilibrium are due to (1) the resistance by friction and adhesion becoming greater as the tube sinks deeper, owing to the larger surfaces in contact; (2) to the forcing up of a column of broken jelly in the cylinder. The latter effect is greater in a narrow cylinder. It was attempted to remove the former by oiling or greasing the rod, but the result could not be made uniform. The best method of working was found to be as follows:—

Having first observed the "bearing weight," *i.e.*, the weight required (tube + mercury or shot) to break the surface, gradually increase it till a weight is found which will force the sinker uniformly through the distance. Place this weight *at once* on another cylinder of jelly, and record the time taken to traverse the distance.

Experiment 1.—Cylinders of different diameters were filled with a 5 per cent. solution of a high grade gelatine, and cooled for two hours in ice and water. The sinker was 11 mm. diameter, the cylinders 22, 24, and 26 mm., hence the annulus of jelly was 11, 13 and 15 mm. The results were:—

A	416	grammes	sank	40	mm.	in 1 minute:	annulus	11 mm.
B	,,	,,		30	,,	,,	13	,,
C	,,	,,		25	,,	,,	15	,,

Mean 100 millimetres in 197 seconds.

It will be noticed that

$$40 \times 11 = 440$$
$$30 \times 13 = 390$$
$$25 \times 15 = 375$$

therefore the effect of the width of the vessel diminishes as the diameter increases, showing that a wide vessel should be

used where possible. Kissling adopts 80 mm. diameter and 120 mm. height.

Experiment 2.—Diameter of sinker. A tube 17 mm. wide, mercury-weighted to 416 grammes in a cylinder of 40 mm. diameter, sank 10 mm. in one minute and then became stationary.

A tube 26 mm. diameter loaded to 815 grammes in a cylinder 80 mm. diameter would not sink into the gelatine at all.

Ten mm. was found to be a convenient diameter.

Experiment 3.—A 2½ per cent. jelly from a second-class gelatine cooled four hours at 20° C. The weight of sinker required was found to be 92 grammes, and the times for sinking 100 mm. were 105, 81 and 99 seconds in three different cylinders of 26 mm. diameter. Mean 95 seconds.

(The 17 mm. sinker of the same weight went down 45 mm. in 170 seconds and then stopped.)

The "bearing weight" required to penetrate the surface of the jelly was

Diameter of Sinker . .	26	17	11	millimetres.
Sectional area of Sinker .	531	226	94	sq. millim.
Bearing Weight. . .	132	69	35	grammes.

The weights required are not proportional to the sectional area. For bearing weight it is advantageous to use a wider sinker than for consistency. The latter is, however, a preferable determination as regards agreement of duplicates, and admits of fair accuracy when carried out under standard conditions. The values of the two gelatines used above would have been recorded as 197 and 95, which is consonant with their other characters.

6. *Weidenbusch*, 1859 : *Breaking Strain of a Rod made of Glue and Plaster of Paris.*—Sticks of plaster cast of uniform size, saturated with glue and dried thoroughly are placed one by one in a metallic ring having notches to

receive them: a lever bears on the centre of the stick as the resistance, and a mercury cup on the long arm forms the weight. Mercury is poured into the cup till the stick commences to break. The weight required is recorded, and compared with a standard glue gives the "Weidenbusch figure". For special purposes where glue is required as a body this would seem to be a practical method, but it is somewhat uncertain.

7. *The Spandau Test.*—Karmarsch proposed, and the Artillerie Werkstätte, Spandau, has adopted, the severing strain of two blocks glued together. They are usually made of well-seasoned mahogany, in America of maple, and the parting is caused by a lever, clamps, and weights, or better by a system of levers in a cement-testing machine. For the important objects of joinery and cabinetmaking this would seem to be an eminently natural process, all the rest being more or less arbitrary and artificial, except with reference to covering power and economy. But by a great number of experiments it was found that the error in duplicates was often very large, as has been remarked by numerous observers. Hence, I undertook an investigation of the causes of inaccuracy. These were found to consist of: (*a*) Inconstancy of material and surface in the blocks to be severed. The following figures are given for holding power in kilogrammes per square centimetre :—

Wood.	Cut Across the Grain.	Parallel to the Grain.
Beech	155	79
Hornbeam	126·5	79
Maple	88	63
Oak	128	55
Fir	110	24

The hold on wood cut parallel to the grain being the same whether the fibres are laid parallel or crosswise.

(*b*) Time of heating the glue and temperature of glueing,

thickness of glue interposed, pressure used (with occasional obliquity in applying the pressure, therefore inequality in the layer), presence of lumps.

(*c*) Moisture in the atmosphere and temperature while setting, and duration of rest before trial.

(*d*) Temperature, etc., while testing.

(*e*) Possible jerking in applying the weight.

Kissling substituted for wood two vertical solid cylinders of nickel-plated iron, with one end smooth and the other with a hook for applying the strain. But there is a great practical objection to using an absolutely non-porous material for the surfaces to be glued. On examining the fracture it will be found that it usually occurs between the glue and the metal, therefore the measurement is simply that of the *adhesion* of the glue to the metal; whereas, in practice, if a joint properly made be examined after rupture, it will be found that the parting takes place through the substance of the glue layer itself, about half of which remains attached to each face of the wood, so that the test is a practical measure of the *cohesion* of the glue. Roughening, lining or grooving of the metallic surface does not remove this objection.

On the other hand, in severing glued wood, it frequently happens that the fracture breaks into the substance of the wood itself, the latter having a lower tenacity than the glue: here the test is obviously valueless.

Bauschinger devised a sliding or lateral test, in which two pieces of red beech wood, a decimetre square, were glued together with their fibres parallel and their surfaces over-lapping one centimetre. The pieces were fixed in a Werder's testing-machine, and forced in a direction parallel to their surfaces, till the glue yielded, and the pieces slid over one another. This test is only advisable for special uses, as friction interferes, and the wood itself frequently breaks; moreover, in joinery, a slide is usually stopped by a mortise.

Horn determined the resistance to a tearing force of the substance itself, as: Common glue, 9·6 kilos per square centimetre; Cologne, 10·6; gelatine, 31·5: this would greatly depend on the hygroscopic state.

For special objects, Setterberg (*Schwed. technisk Tidskrift*, 1898, xxviii., 52) soaks strips of paper in the glue solution, removes the excess with filter paper, allows to dry, and then mounts the strips in a paper-testing machine.

By a large number of experiments I was led to adopt the following process and precautions:—

For the testing blocks a hard yet moderately porous biscuit stoneware was found to be a much better material than wood. They were made to our design by Messrs. Doulton, and were of the shape of a truncated wedge fitting the claws of the machine—a glue-tester by Bailey of Salford, with a system of levers, and a weight tub loaded with shot which was afterwards weighed. The opposing planes showed a fine uniform grain; they were accurately ground to the square inch. After using, they were boiled clean, and dried for further use.

One part of broken glue soaked in 2 parts of cold water for six hours, then raised to 70° C., agitated in a covered vessel till dissolved, and rapidly strained through fine muslin. The plane surfaces were soaked in this for thirty minutes at 70° in a covered vessel, joined carefully with light pressure, the pairs mounted in a frame between uprights, each pair being cautiously loaded with a weight of 5 lb., and the whole kept for five days in a cool and dry room. At the end of that time they were mounted in the machine and tested, the utmost care being taken to avoid jerking, to put on the weight gradually, and to keep the lever horizontal. An improvement on shot would be a hopper with dry sand or mercury flowing through a regulated orifice with an automatic cut-off at the moment of

fracture, which is generally sudden. Supports must be placed just underneath the weight tub.

Example.—A brown Scotch glue of excellent character gave, with four different pairs of stone blocks, a breaking strain of 675 lbs., 636 lbs., 712 lbs., and 645 lbs. per sq. in. The average of all the mahogany blocks (ten experiments) was 331 lbs., but the single experiments varied from 70 lbs. to 668 lbs., showing scarcely any regularity or certainty. The stone, on account of its lower porosity, worked best with 50 per cent. glue, the mahogany with 20 per cent.; a thin film of glue remained attached to both stone surfaces after rupture. The greatest advantage that stone blocks possess is their *rigidity*, the largest source of error in wood blocks being due to the elasticity and compressibility of the wood, and consequent yielding and slipping during the test, which often brings about the fracture prematurely, and occasions abnormally low results.

A rough method of glue testing without apparatus is to cut transversely with a fine saw a stick of wood 5 centimetres (1 inch) square, to glue the cut surfaces together and mount them on end with a moderate weight on top. After three days, the bar is laid across the supports, and weighted gradually in the middle till fracture ensues. Good glue should sustain a weight of at least 75 kilogrammes.

8. *Viscosity or "Body" Test.*—An American manufacturer sends me the annexed description of this process as practised by their firm :—

"One oz. of glue is soaked thoroughly in 10 ozs. of water, melted in the water bath, poured into a 'testing tube' kept at a standard temperature, and the time observed that is taken in running through. 'Water requires 37 seconds while the very weakest glue takes 40 to 43 seconds.' The ratio is the 'body test'—'indicating the consistency of the glue and the amount of surface it will cover, and, therefore, its cheap-

ness in use and good working and water-taking qualities'. We attach more importance to this test than to the consistency of the jelly." The above determination would show a ratio in 10 per cent. solution, taking water as a standard, of $\frac{43}{37}$ for the very weakest glue, or in decimals 1·16.

But in the method of noting the time taken by 50 cubic centimetres of a 10 per cent. solution to run out from a

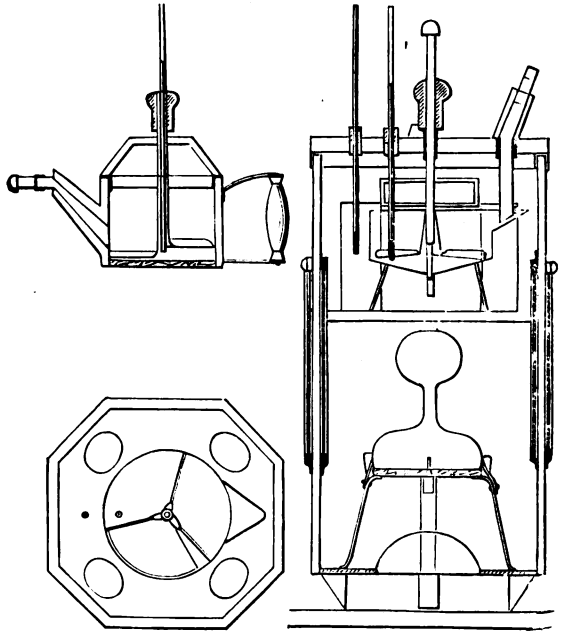

FIG. 13. Engler's Viscosimeter.

burette fitted with a fine jet, as compared with the time taken by water under the same conditions, the numbers obtained are not strictly proportional to the true viscosity, and vary so much with slight differences of temperature that very serious errors may arise if the operator, working on different days, does not use for comparison all the standard glues he had previously employed.

For this reason Julius Fels employs Engler's viscosimeter (improved form, *Journ. Soc. Chem. Industry*, 1890, p. 654) with a 15 per cent. solution, and subjoins this table :—

No.	Description of Samples.	Per cent. of moisture in original.	Time of efflux of 500 cc. at 30° C. in seconds, water taking 90 seconds.	Viscosity
1.	Light yellow transparent thick plates	16·3	149	1·65
2.	Brown transparent glue . .	14·0	125	1·36
3.	Sherry-coloured transparent glue	15·4	171	1·91
4.	Light yellow plates, brittle .	18·2	150	1·60
5.	Muddy (trüber) glue . . .	15·2	199	2·21

He remarks that " the viscosities found agree with the respective behaviours under water. No. 2 became entirely slimy in a few hours and fused into one lump, whereas No. 5 kept its shape, and on scraping with the finger showed scarcely any gelatinisation. Nos. 3 and 5 in twelve hours gave a thick jelly, while No. 2 in twenty-four hours yielded only a poor and thin result."

The ordinary preference for a dark glue is justified by the above figures. No. 2 seems to have been over-dried. Lighter glues may have been bleached at the sacrifice of tenacity.

In determinations of viscosity I use and prefer an apparatus modified from Slotte's form, which I have described and figured in the *Journal of the Society of Chemical Industry*, 1891, p. 615, as being simpler, cheaper, more manageable, and giving the datum in terms of absolute measurement. The numbers given by different observers have been obtained at different temperatures, and with different strengths, hence are not strictly comparable. Thus, Fels worked at 30° C. with a 15 per cent. solution, the Americans with 10 per cent. " at a standard temperature ". Therefore conditions should also be stated. I have been accustomed to use a 1 per cent.

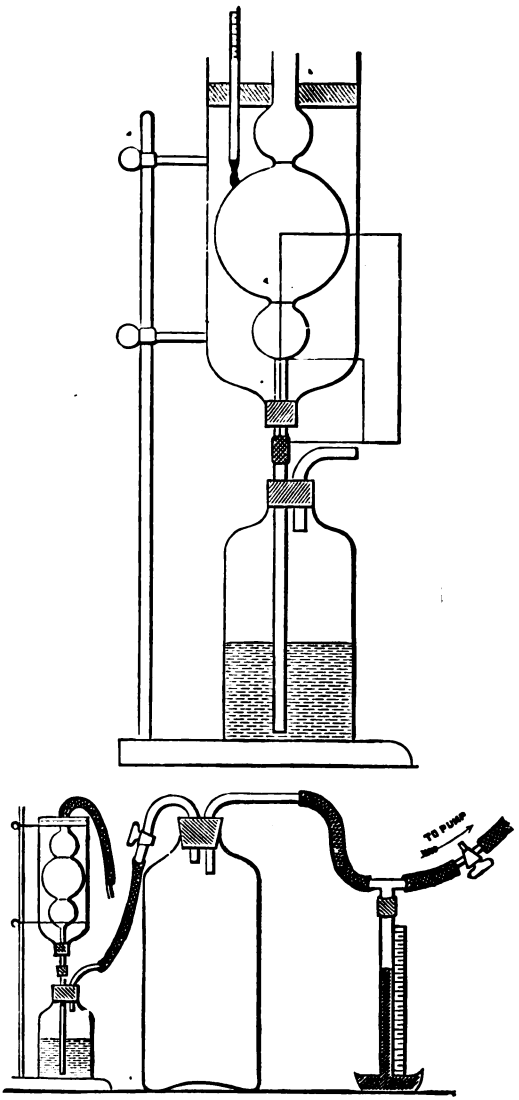

FIG. 14. Rideal-Slotte Viscosimeter.

solution at 18° C., operating in the way mentioned in the above paper.

The three bulbs are kept by the water jacket at the temperature required. The glue solution, also at the right temperature, is drawn up through the capillary tube from the lower bottle till it just fills the upper small bulb. Then the suction tube is removed, the upper glass tube immediately closed with the finger, and the solution cautiously run down to the upper mark of the large bulb. At this point the time is noted, and the liquid at once allowed to run till it reaches the lower mark, when the exact time is again noted. The difference is the number of seconds required to empty the large bulb under atmospheric pressure. For very viscid glues the time may be hastened by applying suction below as shown in the figure. In this case the gauge of the pump must be read and a correction applied, except for immediate comparisons. The complete formulæ and corrections are given in the paper. It is easy from them to make a table for at once translating the data observed into absolute viscosities, or more conveniently, into the relations to water taken as 100.

It is essential to pass the solution first through a capillary tube by pressure to remove lumps, which are more frequent in "muddy" glues—some of the high figures found for this class (*e.g.*, the 2·21 in Fels's table) may be due to this feature. Straining through muslin is not sufficient, but should be used as a preliminary. My figures for different varieties (1 per cent. at 18° C.) have ranged from 1·19 to 1·6.

Kissling has recently given the following table of tests for different glues (*Chem. Zeitung*, xxii. [19], 172):—

Number.	Description.	Price per cwt. in shillings.	Smell of soaked glue.	Consistency of jelly (rod method)	Viscosity of 17 per cent. solution at 25° C.	Non-gelatine percentage (Stelling).
1	Skin glue . . .	44s.	good	over 1000	15	7·6
2	,, . . .	44s.	,,	—	9	8·2
3	,, . . .	48s.	very good	130	4	8·3
4	Bone glue in powder	36s.	fair	5	4·2	14·8
5	,, ,, .	36s.	unpleasant	140	5·5	—
6	,, ,, .	36s.	fair	1	3·7	—
7	,, ,, .	36s.	,,	234	7·4	15·0
8	Mixed glue . .	41s.	bad	1·5	2·8	13·6
9	Bone glue in cakes .	28s.	,,	2·4	—	15·4
10	,, ,, .	26s.	very bad	—	—	23·2
11	,, ,, .	26s.	rather bad	liquid	2·8	15·6
12	,, ,, .	26s.	bad	120	4·4	8·75

This author remarks that "the smell is especially important, as indicative of the keeping properties. (Compare No. 3 and No. 12 above.) In adhesive power cheap bone glues give almost as good results as the high-priced skin glues. If a glue buyer requires good smell, gelatinising property, and freedom from acidity, a best skin-glue must be selected. If only the adhesive properties are to be considered, a cheap bone glue will answer the purpose."

"Fels's method—that is, the determination of the viscosity—can give very useful indications, but there are certain reservations which must be made. Solutions of glue undergo —after a more or less prolonged time of standing—modifications in fluidity. In this way a freshly-prepared solution had a viscosity of 9·0, but after standing for twenty-four hours it had assumed a gelatinous consistency. Another solution underwent the following modifications: Its degree of viscosity was 3·7 after two hours, 4·8 after twenty-four hours, and 5·4 after forty-eight hours."

9. *Foam Test.*—A 10 per cent. solution is beaten or stirred vigorously for three or four seconds with a small glass rod,

the height of the foam measured in inches, and the rate of its disappearance noted. "Some glues show $\frac{1}{2}$ in. foam, some $\frac{1}{4}$ in., $\frac{1}{8}$ in., and some none at all. It does not necessarily follow that there is anything wrong with the glue, but a great many customers object to foam." For some purposes frothing is a great disadvantage.

Valuation of Raw Materials.

The value of glue-making materials, more especially of tanners' "spetches" (refuse and parings), depends not only on the absolute amount of glue-forming substance, but also on its relation to the non-gelatine. Gantter boils 100 grammes of the sample with 1 litre of water and a few drops of soda till completely extracted, makes up to 2 litres, and allows to stand covered in a warm place for ten hours. The insoluble matters settle, while the fat rises to the surface. The residue and ash are determined in 20 cc. (= 1 gramme of substance). Another 20 cc. are diluted, neutralised with acetic acid, precipitated by tannin, filtered, and any excess of tannin withdrawn by hide-powder; the liquid evaporated, dried, and its ash deducted, gives the organic non-gluemaking material.

It may be said in conclusion that a careful inspection of the results of the scientific examinations of a glue or of raw materials gives frequently a better criterion of its value for a definite purpose than the price, as the latter is often determined by hand tests and by artificial considerations.

The following is an example of the examination of two typical glues, with the conclusions derived:—

(1) *Chemical Examination:*—

	Best Glue, 1.	Common Glue, 2.
Moisture . .	14·32 per cent.	13·41 per cent.
Ash . . .	6·04 „	1·77 „

The ash in each case contained lime, phosphoric acid, and chloride indicating the presence of bone glue.

(2) *Mechanical Examination* :—

	Best Glue, 1.	Common Glue, 2.
Water absorbed after soaking in the cold for forty-eight hours.	500 per cent.	170 per cent.
Condition after soaking.	Firm and gelatinous.	Semi-fluid.
Odour of solution after heating.	Slight, inoffensive.	Slight, inoffensive.
Viscosity of 10 per cent. solution at 60° F. compared with that of normal rape oil at the same temperature taken as 100.	Solution too gelatinous to flow.	15.
Tensile strength between test blocks of mahogany, lb. per square inch.	511.	227.

In spite of the slightly higher percentage of water, and the considerably greater amount of ash which it contains, sample 1 is a quality so much superior to that of sample 2 that it would be more economical to buy even at the rate of £38 per ton as against £24 per ton for the other.

From the tensile strength figures, it follows that the best glue is better in the ratio of 13 to 9 per unit price, *i.e.*, for a given sum of money the best glue is 60 per cent. better.

As in many other trades, a great deal of reticence is practised by glue and gelatine manufacturers with regard to the details of their special processes, although in all cases the processes must be broadly the same. But in this work special care and attention to minutiæ is required at every stage, and when by long experience a particular recipe is found to be successful, there is every excuse derived from competition for keeping it carefully concealed. And yet the policy of "trade secrets" has of late years undergone a

considerable change. It has been recognised that the open publication of scientific researches has been of incalculable advantage to manufacture, while it has been also slowly found that many jealously guarded recipes of the "rule of thumb" order were either unnecessary or absolutely detrimental. Communication and discussion of the various processes, such as manufacturers and chemists have established in the "Society of Chemical Industry" has led to great improvement in methods and economy of production, as it has become increasingly evident that scientific precision was indispensable for attaining the best and most uniform results. It is difficult to understand why practical men, especially in the British Islands, so rarely appreciate the advantage of working under exact conditions of temperature, time and quantities. While in the best manufactories attention to these points is very carefully practised, the private workman is usually content with the crudest "rule of thumb" methods, with the result of occasional most irritating failures, which are either wrongly put down to the glue or attributed to the weather or other cause. For makers, buyers and users alike, an intelligent knowledge of the subject is indispensable.

CHAPTER VI.

COMMERCIAL ASPECTS.

As will be gathered from our previous remarks, glue, gelatine and size are looked upon as subsidiary or bye-products to the leather industry, and receive only casual reference in trade journals. For this reason we find no reference specially in the *Board of Trade Journal* or in Consular reports to glue or gelatine as separately tabulated articles of commerce. The importance of these articles to the joinery, cabinetmaking, paper, printing, and other industries, would seem to indicate a different treatment. The fault is largely due to the extraordinary secrecy observed in the glue trade, whereby, while other manufactures have been worked up by scientific investigations to the maximum of efficiency, the making of glue has remained traditional, with local maxims and local errors. For instance, a leading manufacturer writes :—

" The manufacture of glue being in great part a secret one, each manufacturer having different methods of preparing his articles, records of the manufacture are simply matters of knowledge handed down from father to son amongst the head men of the trade ".

Another states that :—

" Every one must make their own experience, which in most cases in our trade has been very dearly bought ".

Consequently, whereas in other greater trades the publicity

has led to scientific researches which have proved of advantage to the production generally, in the glue trade the rather antiquated policy of exclusiveness, secrecy, and dread of competitors has succeeded in keeping the rationale of the processes to a certain extent unknown, the information scanty, and improvement, particularly in the English trade, decidedly backward. "Trade secrets," as a rule, are of very little value, and often, when leading to a stereotyped mode of procedure, are a hindrance to advance. As in other chemical trades, the object is to produce the greatest amount of a definite substance of the highest quality consistent with price. There must be, at most, one or two best ways of doing this: any deviation from these must result in loss, and can only be avoided by a uniform method being, as much as possible, adopted, the precautions carefully worked out and tested with exactness at every stage. This could be done by collaboration, as in other industries, when the glue and gelatine trade would be saved from the minor position, and the uncertainties and fluctuations it has shown in the past.

There is a great difficulty in obtaining statistics of the glue trade. As we have already mentioned, glue, gelatine, size, isinglass and "stock," do not appear in the British Board of Trade Returns, and are probably massed as imports in "raw materials for non-textile industries," and as exports in "miscellaneous" or "other articles". Scanty and scattered information is found in the official reports of foreign countries, most of it discouraging. Thus in a German report of 1893 it is said:—

"The bone meal and glue industry sustained a loss owing to Russian competition and the increased sale of superphosphates" from mineral sources. "Many bone-ash works betook themselves to the manufacture of glue, thus further depressing the position of that industry."

And again in a report of the same country for 1894 :—

"*Glue* lost the Austrian and Dutch markets, but found compensation in England, the States, and English North America; the prices, however, receded from 100 to 70 marks per 100 kilos (£51 to £35 10s. per ton). The imports are valued at 25 marks less (1893; 15 marks), and reached a maximum in 1890, 1734 tons in 1892, and 1958 tons in 1893." In the same report it is stated: "The exports of *gelatine* lost ground in Holland, Belgium, and Russia, but this was more than compensated for by the increased demand in England and the States. There is a simultaneous decrease of imports," with values receding for exports from £157 to £112, and for imports from £147 to £102 per ton.

A prominent member of the trade writes :—

"In England there are certainly no statistics available as to the production of glue, which is an uncertainty, and of regular irregularity." He probably refers to the long-established habit of suspension of work while climatic circumstances are unfavourable. "Works close and open, work in fits and starts. There are bone-glue works—these make, at least some of them, mixed glues also, *i.e.*, hide and bone and horn piths—and purely hide-glue makers. A number of tanners work up into glue their own production of hide pieces. Paper makers work up hide pieces into size for their own consumption. All the world over a similar state exists."

There has always been great competition between the manufacturers of hide and of bone glue. While the former has always been ranked higher in the carpentry and cabinet trade, and has commanded a better price, it has been recognised that, owing to the chemical improvements in the treatment of bones, the glue from them has been nearly equal in tenacity and often better in colour, so as to be more suitable for many purposes, at the same time being sold at a lower price; hide glue averaging about £46 per ton, and bone £35

to £21 or lower. Many other products were also obtained from bones, such as bone meal, superphosphate, fat, animal charcoal, ammonia, bone oil and phosphorus, and were expected to make the process highly remunerative. For a time there was a considerable demand for bone or "patent" glue, especially in France. But glue still remained "a drug in the market" till the latter part of 1896, when an impulse was given to the hide glue trade by the failure of a number of bone glue works in Germany, some of them with large productions. So-called "small cake patent glue," benzene bleached, was thrown on the English market in quantities for cash at prices down to £14 per ton delivered. From that time an improvement dates. The same class of glue rapidly rose to £28 per ton, which is now about the price. At present there is a tendency towards improvement, and larger purchases may be expected both from America and elsewhere. But in spite of the improvements in quality attained by better machinery and closer attention to processes, it is complained that English buyers still continue to take glue by superficial characters, such as shape, fracture or gloss, instead of by real quality, and that in consequence imitations are easily passed off. On the Continent more attention is generally paid.

The trades both in America and Holland are syndicated, so that the production is to some extent controlled. In America, the trust, by avoiding cutting prices and the cost of commercial travellers, is endeavouring to maintain former prices, and so make the business more remunerative.

From the Board of Trade Returns the imports of hides into the British Isles for the last ten years have been :—

Year.	Raw Hides, Dry.		Raw Hides, Wet.	
	Cwts.	Value. £	Cwts.	Value. £
1889	575,158	1,573,132	647,250	1,500,455
1890	455,098	1,191,240	584,948	1,323,176
1891	453,268	1,185,360	555,692	1,251,278
1892	368,191	946,354	540,284	1,136,524
1893	357,118	932,043	589,245	1,248,844
1894	419,205	988,912	608,584	1,242,168
1895	491,547	1,153,757	771,133	1,650,369
1896	369,063	905,427	604,728	1,319,501
1897	557,087	1,413,166	638,668	1,336,991
1898	542,454	1,455,806	694,057	1,450,260

The imports of hides into Liverpool for the week ending July 7th, 1899, are given as : 795 salted River Plate, 11,250 salted Italian, 2,000 salted Brazil, 232 salted Oporto, 1,700 dry African, 400 dry West Coast, 4,728 dry E. Indian Buffalo, 66 bales dry Egyptian. Number of hides in markets at time of auctions, 2,534. Corresponding week in previous year, 2,952.

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